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EFFECTS OF ORGANIC SOLVENTS ON THE PERMEABILITY OF CLAY SOILS

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Grant No: R 806825010

Project Officer

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16. ABSTRACT

Traditionally, water has been used as the fluid with which to measure permeability of compacted clay soils to assess their suitability for lining hazardous waste landfill and surface impoundments. To determine if permeability of the liner is sufficiently characterized by its being tested with water alone, permeability studies were conducted using both water and a spectrum of organic fluids commonly placed in hazardous waste disposal facilities. Four clay soils, including kaolinitic, illitic, and smectitic clay soils, were evaluated with the traditional permeability test using water, and all four were found to qualify for lining hazardous waste disposal facilities on the basis of their having permeabilities lower than 1 x 10^{-7} cm sec^{-1}. However, these same clay soils underwent large permeability increases when permeated with basic neutral polar, and neutral nonpolar organic fluids, and showed potential for substantial permeability increases when exposed to concentrated organic acids. Results of this study indicate a need to test the permeability of clay liners with whatever organic fluids the liner may be exposed.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

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ABSTRACT

Traditionally, water has been used as the fluid with which to measure permeability of compacted clay soils to assess their suitability for lining hazardous waste landfills and surface impoundments. To determine if permeability of the liner is sufficiently characterized by its being tested with water alone, permeability studies were conducted using both water and a spectrum of organic fluids commonly placed in hazardous waste disposal facilities . Four clay soils, including kaolinitic, illitic and smectitic clay soils, were evaluated with the traditional permeability test using water, and all four were found to qualify for lining hazardous waste disposal facilities on the basis of their having permeabilities lower than 1×10^{-7} cm sec^{-1}. However, these same clay soils underwent large permeability increases when permeated with basic, neutral polar, and neutral non-polar organic fluids, and showed potential for substantial permeability increases when exposed to concentrated organic acids.

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SECTION 1

INTRODUCTION

Knowledge of the permeability--a main criterion used to judge whether a compacted soil liner will prevent movement of leachates below or adjacent to a disposal facility--is needed to determine a liner's suitability for use as a containment system. However, little information is available concerning the impact of waste fluids on the permeability of clay liners. Also, no simple permeability test method has been developed that is suitable for use with a range of possible waste fluids. Because a study evaluating the permeability of a range of typical clay soils with a spectrum of potential waste fluids would generate a valuable data base, the following objectives were undertaken:

1. To review briefly the testing and use of clay liners for hazardous waste landfills and surface impoundments.
2. To delineate from available information the physical classes of fluid-bearing hazardous waste, the leachates they generate, and the predominant fluids in these leachates.
3. To summarize the available information on the components of native soils used in constructing compacted clay liners.
4. To evaluate the potential interactions between waste fluids and compacted clay soil liners that may alter the permeability of the liner.
5. To develop a simple, inexpensive, and rapid method suitable for use with a wide range of possible waste fluids, for comparative permeability testing of compacted clay soils.
6. To evaluate the permeability of a range of typical clay soils to a spectrum of potential waste fluids.

SECTION 2

CONCLUSIONS

A delineation of the physical classes of hazardous waste indicated that many contain organic fluids. Furthermore, the organic fluids in these wastes may, in the presence of overburden or hydraulic pressure gradients, permeate the liner of a disposal facility. Leachates generated by the organic fluids in hazardous wastes were found to fall into four major categories: acidic, basic, neutral polar, and neutral nonpolar organic fluids.

Permeability remains the primary criterion for evaluating the suitability of clay liners for the lining of hazardous waste disposal facilities. Permeability of clay liners has in the past been determined by using a standard aqueous leachate such as 0.01N $CaSO_4$. Since clay liners may be exposed to organic fluids, a testing procedure was developed to compare the effects of a standard leachate and organic fluids on the permeability of clay liners.

Evaluation of the clay soils used to construct liners showed that the predominant clay minerals in these soils are smectite (montmorillonite), illite, and kaolinite. Four native clay soils that contain these clay minerals were selected for evaluation of the comparative permeability procedures.

When clay soils used in this study are evaluated only by the traditional permeability test using water (0.01N $CaSO_4$), all four would qualify for lining hazardous waste disposal facilities on the basis of their having permeabilities lower than 1×10^{-7} cm sec^{-1}. But these same clay soils underwent large permeability increases when permeated by basic, neutral polar, and neutral nonpolar organic fluids, and they showed the potential for substantial permeability increases when exposed to concentrated organic acids.

RELATIVE PERFORMANCE OF THE FOUR CLAY SOILS

Of the four clay soils studied, the noncalcareous smectitic clay soil showed the lowest initial permeability but the least resistance to increases in permeability when exposed to organic fluids. The calcareous smectitic clay soil had intermediate initial permeability, but it showed a much larger resistance to permeability changes than its noncalcareous counterpart. The result was that the noncalcareous clay generally had a higher final permeability than the calcareous smectitic clay soil. In addition, of the two smectitic clay soils, the noncalcareous tended to yield organic fluids in the effluent after less fluid had passed through the soil.

Though the kaolinitic clay soil had the highest initial permeability of the four soils studied, it nearly always showed the greatest resistance to permeability changes. Organic fluids generally appeared in the effluent of this soil after passage of greater fluid volumes than with the illitic or noncalcareous smectitic clay soils.

The illitic clay soil had both intermediate initial permeability and resistance to permeability changes. But the organic fluids tended to appear in the effluent of the illitic clay soil after passage of less fluid than with the other clay soils.

Overall, the kaolinitic and calcareous smectitic clay soils performed best of the four clays studied. These two clays showed greater resistance to permeability increases, and organic fluids appeared in their effluent after passage of more fluid (larger pore volume values) than the illitic or noncalcareous smectitic clay soils. Note, however, that all four clay soils showed permeabilities greater than 1×10^{-7} cm sec^{-1} when exposed to several of the organic fluids tested.

RELATIVE EFFECTS OF ORGANIC FLUIDS ON PERMEABILITY OF CLAY SOILS

Organic acids apparently affect permeability by different mechanisms than other organic fluids studied. The operative mechanisms for permeability changes with acetic acid appeared to be dissolution of soil particles followed by piping of the particle fragments through the soil. A sharp initial permeability decrease resulted as the migrating particle fragments clogged the fluid conducting pores. However, permeability increased gradually (with two of the soils) as the acid dissolved soil particles that clogged the pores.

No dissolution or piping was observed for the soils permeated by the weak organic base (aniline) or the neutral organic fluids. These fluids tended to cause permeability increases by means of altering the structural fabric of the soil.

Neutral nonpolar fluids caused initial permeability increases of approximately two orders of magnitude. The soils so treated tended, however, to reach relatively constant permeability at that point. The basic and neutral polar fluids showed continuous permeability increases with no apparent tendency to reach maximum values. Though the large viscosity of ethylene glycol and aniline slowed the rate at which these fluids increased permeability relative to less viscous acetone and methanol, all four fluids increased permeability of soils as compared to values obtained with water (0.01N $CaSO_4$).

A potential exists for the data reported here to be taken out of its laboratory context and related back to the field. The data presented here should not be used as a definitive data base for time-to-failure analysis of clay liners. It should be noted that in the literature search performed no data were found on field verification tests of the impact of organic fluids on the permeability of clay liners. All clay liner qualification tests identified in the literature have been laboratory scale using various permeameter designs.

Because of the above related effects, the results of this study indicate the need for testing the permeability of clay liners with the organic fluids to which the liner may be exposed. Permeability tests using the actual fluids present in a waste would be an environmentally sound alternative to tests using water only.

SECTION 3

STATE-OF-THE-ART-REVIEW

HAZARDOUS WASTE LAND DISPOSAL OVERVIEW

RCRA regulations concerning hazardous waste disposal facilities (effective November 19, 1981) prohibit the landfill disposal of drums containing free liquids (EPA, 1980a). Furthermore, the regulations prohibit the disposal of bulk liquids in hazardous waste landfills unless the landfill has an "adequate liner" and a "leachate collection and removal system" (EPA, 1980b). Morrison (1981) indicated state hazardous waste regulations have done little to stem the disposal of organic liquids in landfills and surface impoundments.

According to a nationwide industry-sponsored survey of land disposal practices, the United States has a total of 12,627 active landfills. Of these landfills, 40 were reported to operate with liners and only 26 were listed as having an operational leachate treatment and control process (National Solid Waste Management Association, 1981). The majority of active landfills are municipal in nature and usually do not accept industrial waste (Table 1). In addition, the survey of land disposal practices identified 109,839 active industrial waste surface impoundments of which 69,490 are on-site facilities. No information was reported on the number of these surface impoundments that have liners or active leachate control.

Approximately 15% of all industrial waste (57 million metric tons, wet weight, per year) is classified as hazardous (Hanrahan, 1979; EPA, 1980c). EPA-sponsored industrial studies conducted from 1975 through 1978 indicated that 78% of all hazardous waste in the United States is disposed of in unlined landfills or surface impoundments, whereas only 2% is disposed of in "secure landfills" (EPA, 1980c).

Cheremisonoff et al. (1979) estimated that 90% by weight of industrial hazardous wastes are produced as liquids. These liquids are further estimated to contain solutes in the ratio of 40% inorganic to 60% organic. The heterogeneous nature of hazardous waste greatly complicates attempts to predict its possible effect on such parameters as permeability of clay liners. However, much can be gleaned from extensive lists of typical descriptions given for the content of drums placed in industrial landfills (Table 2).

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TABLE 1. PERCENTAGES OF INDUSTRIAL VERSUS MUNICIPAL LANDFILLS REPORTED IN THE STATES OF GEORGIA AND WASHINGTON*

State	Industrial Landfills		Municipal Landfills	
	No. in State	% of Total	No. in State	% of Total
Georgia	125	24	392	76
Washington	100	44	126	56

* National Solid Waste Management Association, 1981.

TABLE 2. TYPICAL DESCRIPTIONS OF THE CONTENTS OF DRUMS PLACED IN INDUSTRIAL LANDFILLS*

Dibromo propanol
Methylene chloride bottoms
Fractional bottoms
Pesticides
Distillation bottoms
PCB waste
Oil sludge
Solvent bottoms
Chlorinated still bottoms
Trichlor bottoms
Ink sludge
Phenol sludge
Paint sludge
Tank sludge
Still residues
Organic residues
Terephthalate sludge
PCB bottoms
Laboratory chemicals
Sulfonated still bottoms
Heavy metal sludge
Chlorinated solvent sludge
Mercury filter press sludge
Tank bottom residues
Still bottom residues
Chlorinated organic residues
Plating sludge
Urethane lacquer
Toluene still bottoms
Methanol slurry
Resinous sludge
Phenol tar sludge
Fuel oil sludge
No. 6 fuel oil sludge
Contaminated fuel oil
Glycol waste
Heat transfer oil sludge
Acetic acid sludge
MEK distillation bottoms
Liquid resins
Freon bottoms
Oil and grease sludge
Miscellaneous liquid wastes
Chlorinated xylene sludge
Benzyl alcohol bottoms
Grinding oil sludge
Filter sludge
Transformer oil sludge
Methyl chloroform bottoms
Organic sludges
Perchlor bottoms
Waste solvents
Resins and solvents
Mixed solvents

* Source: Public Records of the State of New York on Chem-trol Pollution Services Scientific Landfill No. 3 containing approximately 680,000 ft^3 of industrial waste.

PHYSICAL CLASSES OF HAZARDOUS WASTE

Land disposal of hazardous wastes can be categorized into the following four physical classes: aqueous-inorganic, aqueous-organic, organic, and sludges. This categorization was used, for example, in a report to Congress (EPA, 1974) (Table 3).

Aqueous-inorganic is the class of wastes in which water is the solvent (dominant fluid), and solutes are mostly inorganic. Examples of these solutes are inorganic salts, metals dissolved in inorganic acids, and basic materials such as caustic soda. Examples of wastes in this category are brines, electroplating wastes, metal etching wastes, and caustic rinse solutions.

Aqueous-organic is the class of wastes in which water is solvent and solutes are predominantly organic. These solutes are polar or charged organic chemicals, as inferred by their water solubilities. Examples of this class of waste are wood preserving wastes, water-based dye wastes, pesticide container rinse water, and ethylene glycol production wastes.

Organic is that class of wastes in which an organic fluid is solvent and the solutes are other organic chemicals dissolved in the organic solvent. Examples of this class of wastes are oil-based paint waste, pesticide manufacturing wastes, spent motor oil, spent cleaning solvents, and solvent refining and reprocessing wastes.

Sludges represent the fourth class of wastes. They are generated when a waste stream is dewatered, filtered, or treated for solvent recovery. Sludges are characterized by high solids content such as found in settled matter or filter cakes and consists largely of clay minerals, silt, precipitates, fine solids, and high molecular weight hydrocarbons. Examples of this waste are API separator sludge, storage tank bottoms, treatment plant sludge, or filterable solids from any production or pollution control process.

TABLE 3. PHYSICAL CLASSES OF HAZARDOUS WASTES

Waste Class	Solvent Phase	Solute Phase
Aqueous-inorganic	Water	Inorganic
Aqueous-organic	Water	Organic
Organic	Organic fluid	Organic
Sludges	Organic fluid or water	Organic and inorganic

Both economic and pollution control pressures continue to mandate solvent recovery and reductions in discharges of fluid wastes. These factors have and will continue to make sludges the fastest growing class of wastes. After placement of sludges in a waste disposal facility, leachates migrate out of the sludge due to gravitational forces, overburden pressures, and hydraulic gradients. These leachates are similar in physical form to the first three classes of waste shown in Table 3.

LEACHATE GENERATED BY HAZARDOUS WASTE

To determine the effect of a specific waste on permeability of a specific clay liner, two unique leachates must be investigated. These leachates include both the flowable constituents of the waste and flowables generated from percolating water leaching through the waste (Fig. 1).

Flowable constituents of a waste, hereafter referred to as the primary leachate, includes both fluids in the waste, i.e., the solvent, plus all components dissolved in the solvent, i.e., the solutes. Depending on the physical class of a waste, its primary leachate may be aqueous-organic, aqueous-inorganic, or organic. Leachate generated from water percolating through a disposal facility is composed of water, the solvent, and all components dissolved or carried with it, the solutes. This

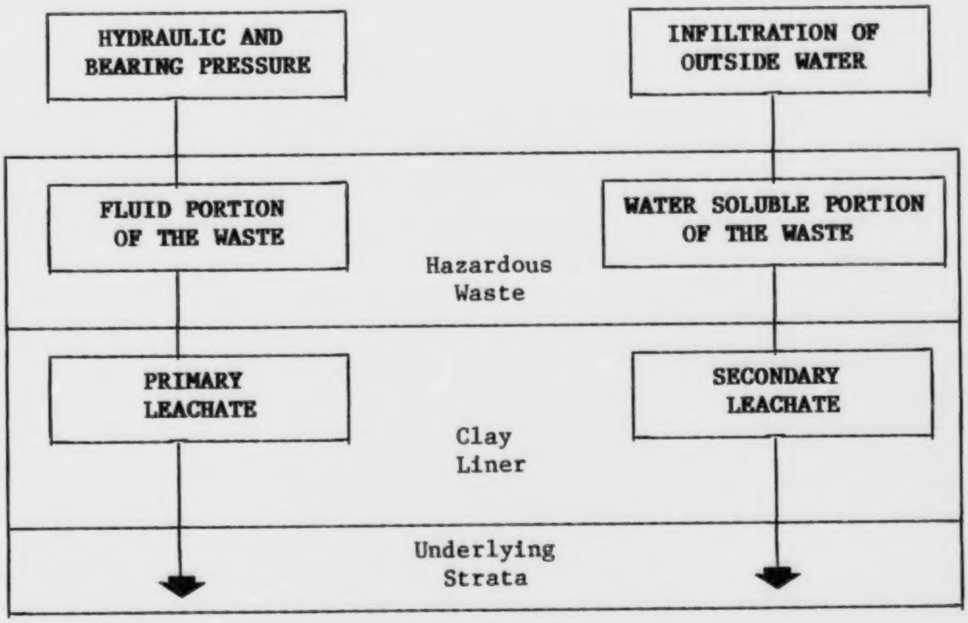
HYDRAULIC AND BEARING PRESSURE
INFILTRATION OF OUTSIDE WATER
FLUID PORTION OF THE WASTE
WATER SOLUBLE PORTION OF THE WASTE
Hazardous Waste
PRIMARY LEACHATE
SECONDARY LEACHATE
Clay Liner
Underlying Strata

FIG. 1. Sources of Leachate Generated by Hazardous Wastes that May Come in Contact with Clay Liners

flowable mixture, hereafter referred to as secondary leachate, may be aqueous-organic or aqueous-inorganic, depending on waste composition.

The predominant fluid or solvent phase of leachates may be water or an organic fluid (Fig. 2). Corresponding solutes in leachates are chemicals that dissolve in the solvent phase. As in the physical classes of wastes, both primary and secondary leachates are divided into a solvent phase, the predominant fluid component, and a solute phase, components dissolved in the solvent (Fig. 3 and 4). While solutes in leachates may affect permeability of a clay liner, the solvent phase will usually exert a dominating influence on permeability.

Essentially all available literature describing leachates generated by hazardous waste disposal only considers water as the solvent (McDougall et al., 1979; Chian and DeWalle, 1977). Water is viewed as a carrier fluid and organic chemicals are considered to be present in only trace quantities. While this may be the case at the interface of secondary leachate and a water table, the fluid phase at the interface of primary leachate and a clay liner will depend on the physical class of the waste being disposed. An organic waste or sludge with an organic fluid phase will most probably expose the clay liner to the organic fluids contained in the waste. As can be seen from Table 2, the organic fluids disposed in a typical hazardous waste landfill cover the spectrum of chemical species.

The scheme presented above for the classification of leachates was previously discussed by Anderson (1981). While this scheme divides leachates into fluid and dissolved phases, there may also be a suspended phase. An example of such a suspended phase would be represented by the inorganic pigments suspended in an organic fluid saturated with paint.

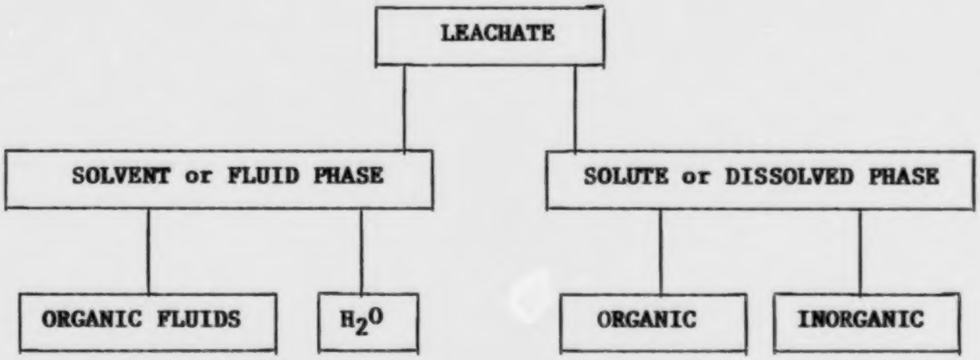

FIG. 2. Composition of the Leachate Generated by Hazardous Waste

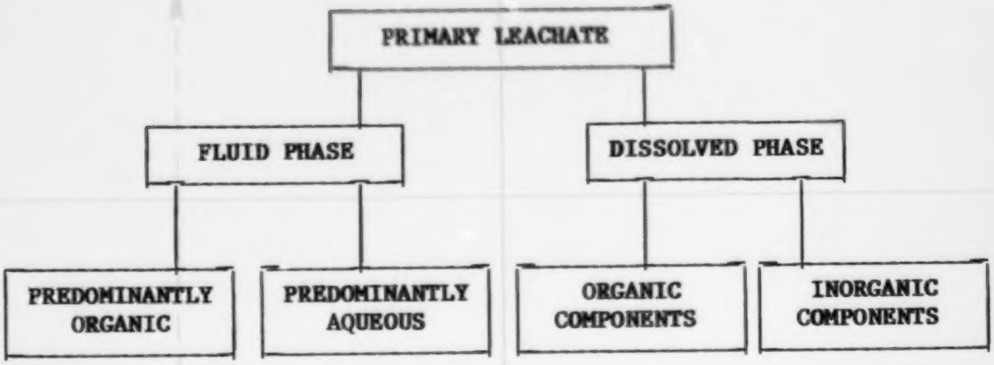
PRIMARY LEACHATE
FLUID PHASE
DISSOLVED PHASE
PREDOMINANTLY ORGANIC
PREDOMINANTLY AQUEOUS
ORGANIC COMPONENTS
INORGANIC COMPONENTS

FIG. 3. Primary Leachate Generated at Hazardous Waste Disposal Sites

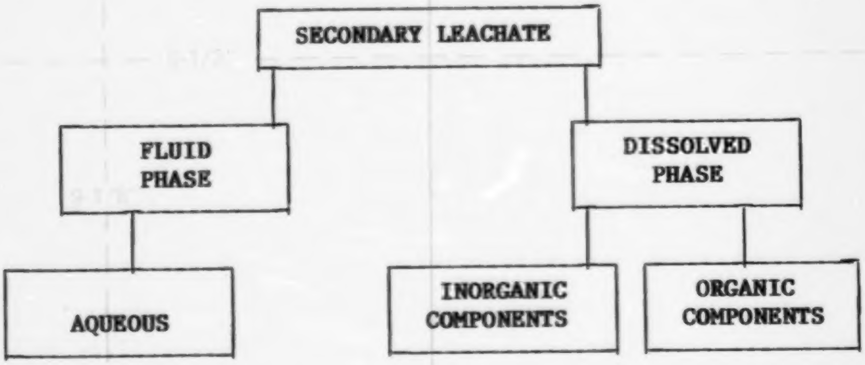
SECONDARY LEACHATE
FLUID PHASE
DISSOLVED PHASE
AQUEOUS
INORGANIC COMPONENTS
ORGANIC COMPONENTS

FIG. 4. Secondary Leachate Generated at Hazardous Waste Disposal Sites

FLUIDS IN HAZARDOUS WASTE LEACHATE

For the purpose of experimentally evaluating effects organic fluids may have on permeability of clay soils, the fluids have been classified into four groups. These groups are based on the physical and chemical properties that govern their interactions with clay minerals. These properties include acidity, basicity, and polarity (Fig. 5). As clay liners are initially wetted with water, the interaction of organic fluids with clay minerals are viewed in the context of fully hydrated clay minerals.

Regardless of type of organic fluid, if it has low viscosity, it may be leachable. Fluids with low viscosity are "by their very nature" leachable and able to extract organic components from other wise dry waste (Wolstenholme, 1977). However, several other fluid properties affect

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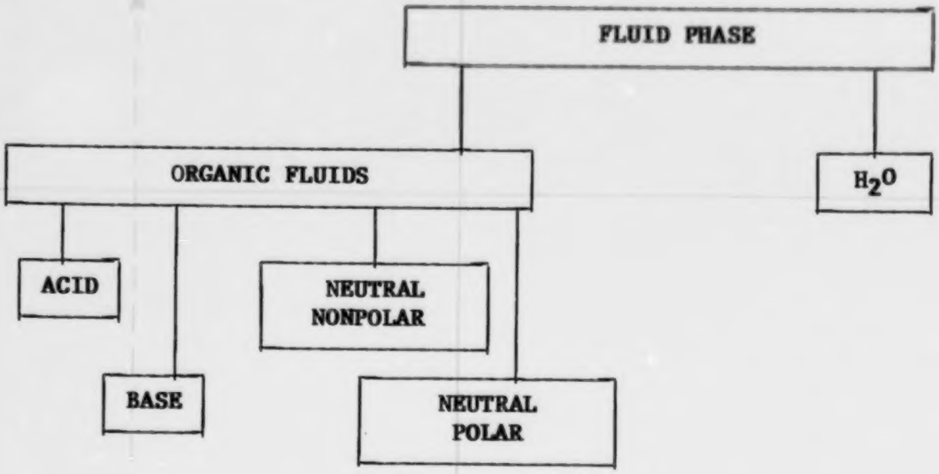

FIG. 5. Classification of the Fluid Phases of the Leachates Generated by Hazardous Waste

resultant soil permeability. Some of these properties are discussed with respect to the four groups of organic fluids and water in following sections.

Organic Acids

Organic acids are organic fluids with acidic functional groups such as phenols and carboxylic acids. Proton donating properties of Bronsted acids give these fluids potential to react with and dissolve clay soil components.

Dissolution of clay minerals in aqueous solutions of organic acids takes place by three mechanisms as follows (Yariv and Cross, 1979):

1. Through cation exchange, a proton replaces an adsorbed cation from the clay surface as follows:

$$Na^{+}\text{-Clay} + HOH \rightleftarrows H^{+}\text{-Clay} + NaOH$$

2. Hydrogen atoms adsorbed to clay catalyze depolymerization of the tetrahedral and octahedral layers;

3. Hydrogen atoms diffusing into the lattice structure replace the structural Al, Mg, and/or Si atoms. These reactions are concentrated at defects in the lattice structure or at nucleophilic sites of isomorphous substitution.

Rates of clay dissolution increase with increasing acid concentration, clay surface area, and MgO content of the clay interior. Dissolution also increases with decreasing particle size, proportional to the square root of time and linearly related to the extent of octahedral substitution (Shainberg et al., 1974).

Kaolinite, illite, and smectite are sparingly soluble in deionized or distilled water (Bar-On and Shainberg, 1970; Huang and Keller, 1973) but are considerably more soluble in dilute solutions of organic acids similar to components of humic acids (Huang and Keller, 1971). Yariv and Cross (1979) identified four ways such organic acids could affect solubility of clay minerals, as follows:

1. Carboxylic acids replace weaker silicic acids that form the tetrahedral layer in clay minerals.
2. Strongly chelating acids such as several of the dicarboxylic and hydroxy acids form stable, soluble, and negatively charged coordination complexes with Al, Fe, and Mg which would increase the solubility of these clay lattice structural components.
3. Acidic organic reducing agents convert metallic oxides into their more soluble hydroxide forms (i.e., ferric oxide → ferrous hydroxide).
4. Acidic organic compounds act as clay flocculating agents which would reduce the effective surface area of the clay mineral and thereby reduce its solubility.

Pask and Davis (1945) boiled several clay minerals in acid (20% H_2O SO_4) and found the percent solubilization of alumina was 3% from kaolinite, 11% from illite, and 33 to 87% from smectite. Grim (1968) found that solubility of clays in acid "varies with the nature of the acid, the acid concentration, the acid-to-clay ratio, and the temperature and the duration of treatment." He also found that the action of acid on clay was enhanced when the acid had an anion about the same size and geometry as a clay component. This would permit even weak acids to dissolve clays under some conditions.

Hurst (1970) found that permeability of geologic formations could be increased by pumping in acetic or formic acid. Johansen et al. (1951) reported flow increases for water wells following treatment with a citric acid solution. Grubbs et al. (1972) found acid waste as probable causal agent in permeability increase of carbonate-containing minerals. X-ray diffraction studies of four clay minerals injected with acid waste showed them to be either dissolved or completely altered. Diffraction peaks showed most variability with smectitic clays.

Organic acids in a deep-well injected waste were the major factor involved in dissolution of smectitic, illitic, and kaolinitic clay minerals (Malcolm et al., 1975). The kinetics and mechanisms for dissolution of smectites by a variety of acids have been described by various authors (Novak and Cicel, 1978; Carson et al., 1976).

An ever present source of organic acids in waste impoundments is anaerobic decomposition byproducts. These include acetic, propionic, butyric, isobutyric, and lactic acids. Anaerobic decomposition yields carboxylic acid derivatives of whatever organic fluids are placed in the impoundment.

Acidization is the name used for the process of increasing the permeability of a porous medium by acid mineral dissolution. This process is widely used to increase permeability and hence productivity of oil wells (Sinex, 1970).

Material that incrusts at the base of wells used for deep-well waste injection usually consists of calcium, magnesium, and iron carbonates, along with imbedded sand and clay particles. To remove carbonate compounds, they must be dissolved and held in solution against precipitation forces. Dissolution is usually accomplished with a stong acid. Calcium will reprecipitate as calcium sulfate in the presence of sulfuric acid, unless it is chelated and removed by a flowing fluid. Chelating agents effective at preventing reprecipitation of various carbonates are citric acid, tartaric acid, and glycolic acid (Anonymous, 1977).

Organic Bases

Bronsted organic bases are organic fluids capable of accepting a proton to become an ionized cation. Since these fluids are positively charged, they adsorb strongly to the negatively charged clay surfaces. Through adsorption, these fluids may replace adsorbed water which would alter the chemistry of the clay surface and change the behavior of the clay soil. While it is not clear if organic bases are strong enough proton acceptors to do so, inorganic bases are known to dissolve certain components of clay minerals.

Bases have been implicated in the dissolution of clay liners. Haxo, Jr. (1976) found in preliminary tests that smectitic clay liners allow passage of both strong acids and strong bases within a short period of time. Nutting (1943) showed that even extremely dilute solutions of alkali effectively removed silica from smectites by dissolution of the crystal lattice.

Industrial sludges, such as still bottoms, crude tank bottoms, and API separator sludges, contain significant amounts of compounds with polycyclic condensed ring structures. These compounds often contain basic nitrogen groups in their ring structures (nitrogen heterocycles). When put in contact with clay minerals, the protonated, positively charged nitrogen groups are electrostatically attracted to the negatively charged clay surfaces. As these basic organic compounds approach the clay surface, two other forces of attraction come into play. First, their large molecular weights would generate strong van der Waals attractive forces. Secondly, there would be interactions between the pi electrons on the aromatic groups with either the exchangeable cations or the oxygens on the surface of the clay (Clementz, 1976). Adsorption of these compounds by clays has been found to be rapid and nearly irreversible while yielding a porous matrix that is structurally stable under either aqueous or organic fluid flow.

With adsorption of organic cations, the charge density of the clay will affect the resulting interlayer spacing. Weiss (1958) found the interlayer spacing after exposure to alkylammonium ions to be 1.3 nm, 1.9 nm, and 2.76 nm for smectites with low, medium, and high charge densities, respectively.

Neutral Polar Organics

Neutral polar organic fluids do not exhibit a net charge but have an asymmetrical distribution of electron density resulting in an appreciable dipole moment (an indicator of polar character) (Debye, 1929). This property allows polar compounds to compete with water for adsorption sites on the negatively charged clay surfaces. As was indicated in the case of organic cations, the adsorption of an organic fluid to clay surfaces will change the behavior of the clay soil. This altered behavior may include changes in permeability of the clay. Examples of such polar compounds are alcohols, aldehydes, ketones, glycols, and alkyl halides.

Grubbs et al. (1973) found that a neutral polar organic, methanol, increased permeability of a core previously injected with oil-based wastes. He also noted use of solvents, organic acids, surfactants, alcohols, and emulsion breakers for permeability enhancement in deep well injection operations.

Brant (1968) found an increase in the permeability of a soil to water after treatment with 4-t-butylcatechol. He postulated that the permeability increase was due to the soil matrix being rendered more stable to water flow. This increased soil stability caused a decrease in migration of soil particles that would have otherwise clogged soil pores.

Neutral polar organic fluids tend to reduce surface tension exhibited by water. The decrease in surface tension (and hence viscosity) of a fluid would significantly increase permeability of a soil as measured with that fluid. Letey et al. (1975) found that permeability of a soil increased with time if there were substances in the soil that were miscible with and decreased the surface tension of water. Additionally, Miller et al. (1975) found that permeability of a soil increased as water flushed out an earlier application of a surfactant.

MacEwan (1944; 1946) demonstrated that a wide variety of polar organic fluids would adsorb to the center layer surfaces of both smectites and halloysites. Theng (1974) found that polar compounds can be adsorbed to these surfaces by van der Waals forces including hydrogen bonding and dipole-dipole interactions. Additionally, these compounds can be adsorbed through ion-dipole interactions with the exchangeable cations of the clay.

Neutral Nonpolar Organics

Neutral nonpolar organic fluids have no net charge and small if any dipole moments. These fluids have low water solubilities and little polarity with which to compete with water for adsorption sites on clay minerals. However, in the presence of a hydraulic gradient, nonpolar fluids move downward through a clay without being appreciably attenuated by clay minerals. Examples of nonpolar organic fluids are aliphatic and aromatic hydrocarbons.

Van Schaik (1970) found that the permeability of three soils was consistently higher for a neutral nonpolar oil than for water. Michaels and Lin (1954) obtained small permeability increases in a kaolinitic clay when a polar permeant fluid was replaced with a nonpolar fluid. They found that the permeability increase was greatest (10-30%) when the polar fluid being replaced was water.

In a study of permeability of a clay subsoil underlying a proposed landfill site, White (1976) found the clay soil to be highly impermeable to water and very permeable to lighter hydrocarbons. The study concluded that "under optimum compaction, a three foot liner of the clay in a tank 23 feet deep containing benzene can begin to leak within 36 days." If the clay soil was compacted at moisture contents below 31%, it was considerably more permeable to the neutral nonpolar fluid benzene.

A significant factor in the initial displacement of water from a compacted clay by a neutral nonpolar organic fluid is the interfacial energy that would exist between the two relatively immiscible fluids. Lambe and Whitman (1979) mentioned this interfacial energy as the reason why, according to these authors, oil can be stored with "no leakage" in prehydrated clay lined reservoirs. While this may be the case for the short term storage of a homogenous neutral nonpolar organic fluid, its validity for the heterogeneous fluids present in hazardous waste has not been determined.

Certain neutral nonpolar fluids (n-paraffins) have been shown to adsorb to interlayer spaces in smectites (Barrier and McLeod, 1954). The usual mechanism for adsorption of nonpolar compounds is by physical adsorption (i.e., van der Waals forces) (Theng, 1974).

Water

Water is a unique fluid in several ways. It exhibits a large dipole moment which allows it to strongly adsorb to clay surfaces. The ability of water to hydrogen-bond to itself permits it to adsorb in multiple layers on clay and form large hydration spheres around inorganic soil cations. These properties give water the ability to cause certain clay soils to swell and seal upon hydration and shrink and crack if water is displaced or extracted from the clay. The role of water in volume changes of clay soils is further discussed in a later section. As mentioned earlier, clay surfaces in a clay liner are initially water-wet. If however, a percolating organic fluid has a higher affinity for the clay surface than water, the clay may become organic-wet (Raza et al., 1968). For example, water and oil are said to compete with each other for solid surfaces in oil reservoirs. A quantitative measure of the preferential wettability of a clay surface for water and an organic fluid can be represented as the difference between the water-clay and organic-clay interfacial energies by the Young-Dupre equation (Adams, 1941) as follows:

$$(\gamma\mathrm{org:c}) - (\gamma\mathrm{w:c}) = (\gamma\mathrm{org:w})\,(\cos\theta)$$

where:

$\gamma\,\mathrm{org:c}$ = interfacial energy between organic and clay (dynes/cm)

$\gamma\,\mathrm{w:c}$ = interfacial energy between water and clay (dynes/cm)

$\gamma\mathrm{org:w}$ = interfacial energy between organic and water (dynes/cm)

θ = angle at the organic:clay:water interface measured through water (degrees)

There is no direct method for measuring either organic:clay or water: clay interfacial energies (Raza et al., 1968). Their difference, however, is equivalent to the product of the water:organic interfacial energy and the cosine of the water:clay:organic contact angle, θ (Fig. 6). This contact angle is easily calculated from capillary rise measurements of the fluids (Baver et al., 1972).

Since the clay surface is negatively charged, polar or positively charged organic leachate components will have an affinity for interlayer surfaces of an expandable lattice clay. Water on the clay surface may be several layers thick, and thus water solubility will improve access of an encroaching fluid to the clay surface. The strength with which water binds to a clay surface will vary with cations adsorbed and clay charge density. However, these factors may change from one place to another in a clay liner. Reviews of interactions between interlayer water and clay minerals recently have been published by Low (1979), Low and Margheim (1979), and Theng (1974).

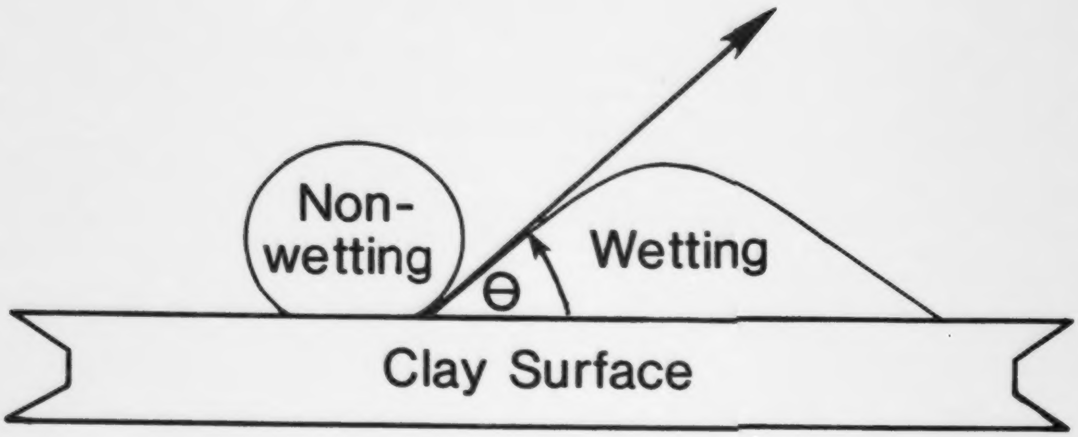

FIG. 6 Contact Angle (θ) Between the Fluids and the Clay Surface

COMPONENTS OF CLAY SOILS

Physically, a clay soil is a porous mixture of air, water, organic matter, and inorganic minerals. Volumetrically, a clay soil contains approximately 40% pore space (occupied by air and water) and 60% solids. The solids contain trace to 15% organic matter and 85% to greater than 99% inorganic minerals. In clay soils, these inorganic minerals are sand (0.05-2.0mm) and silt-sized rock fragments (0.02-0.05mm) and at least 35% clay-sized particles (<0.002mm). These clay sized particles consist of rock fragments smaller than silt and a variety of clay minerals.

Pore Space

Pore space in clay soils is largely determined by the structural arrangements of solid soil components. Pore size distribution determines permeability of clay soils to fluids. While holding total porosity constant, a shift in pore size distribution toward more macropores and fewer micropores greatly increases permeability of clay soils. According to Poiseuille's equation, volumetric flow through porous media increases with the fourth power of pore diameter (Brady, 1974). For instance, where all other factors are held constant, a 1mm diameter pore will conduct volumetric flow 10,000 times that of a 0.1mm diameter pore. According to Dixon (1971), "flow tends to follow the path of least resistance or through large soils voids. . . ." If leachate fluids interact with a compacted clay soil in a way that increases the number or diameter of macropores, large permeability increases would result. Thus, an increase in macropore size was thought to be the reason for permeability increases observed in six California soils following an increase in leachate salt concentration. Waldron and Constantin (1968) noted that the relationship between macropore size and permeability was consistent with "the well-known fact that pore size distribution rather than total pore volume governs . . . permeability." Similarly, large pore formation was determined to be the cause for permeability increases in porous media treated with acids (Schechter and Gidley, 1969). Acid is commonly injected into oil wells to increase the permeability of an oil bearing formation in the region of the well bore.

Structural development has long been considered to be responsible for the presence of large pores in clay soils (Lauritzen and Stewart, 1941). A major force behind structural development is the shrinking and swelling that clay soils undergo with changes in water content. Consequently, if an organic leachate displaces or extracts water from a clay soil, there may be an increase in both the number of macropores and thus permeability.

Pore size distributions and total porosity of smectitic, kaolinitic, illitic, and halloysitic subsoils and commercial clays were determined by Diamond (1970) using the mercury intrusion porosimeter. This method of evaluating pore size distribution is based on the principle that non-wetting fluids, i.e., fluids with contact angles (θ) (Fig. 6) greater than 90° for the solid phase, will only enter a given size pore if sufficient pressure is applied (Washburn, 1921). Thus, mercury is forced under pressure into the dehydrated and evacuated soil sample. Applied pressure is increased incrementally while the volume of mercury entering the soil is recorded. A pore size distribution curve is obtained by plotting pore size against cumulative pore volume while using the following relationship to convert pressure applied to pore radius (Nagpal et al., 1972):

$$P = 2 \lambda \cos \theta / r$$

where:

P = applied pressure

λ = surface tension of mercury

θ = contact angle of mercury

r = pore radius

Another method for determining the pore size distribution of soil is the pressure plate technique. This method is based on the incremental increase of suction on a soil required to remove water from progressively smaller pores. The equation used above also applies to the pressure plate methods where the variables are suction (P), surface tension of water (λ), contact angle of water (θ), and pore radius (r). This technique is less suitable than mercury intrusion because many clay soils experience changes in pore size distribution with changes in water content (Brewer, 1964).

Diamond (1971) investigated the influence of moisture content during impact compaction of illite and kaolinite on pore size distribution.

Either clay, when compacted on the dry side of optimum moisture*, exhibited more large pores than when compacted on the wet side of optimum moisture.

A hydraulic head (h in cm of H_2O) has been shown to displace water in a pore with an equivalent radius (in micrometers) of approximately 0.15h (Marshall, 1959). Where water is being displaced by an immiscible or non-wetting fluid, there would be an additional energy barrier retarding the displacement of water equal to the interfacial energy between the two fluid phases.

An extensive review of pore space in soils and mechanisms of pore formation in relation to soil structure and fabric has been published by Brewer (1964). The publication also covers principles of fabric analysis, classification of voids, and techniques for structural analysis.

Soil fabric or structure has been defined as the physical constitution of a soil material as expressed by the spacial arrangement of the solid particles and associated voids (Brewer, 1964). Voids, interconnected spaces between the solid components, are classified according to their size, shape, arrangement, and morphology.

One size classification scheme for soil voids includes macrovoids ($>75\,\mu m$), mesovoids (30-$75\,\mu m$), and ultramicrovoids ($<5\,\mu m$). The minimum value for macrovoids ($75\mu m$) was chosen to correspond with theoretical minimum diameter pores from which water would be displaced under a suction or hydraulic head of 40 cm of water (Brewer, 1964).

Shape classification schemes for soil voids include those that deal with both coarse characteristics and minute surface details. Examples of coarse characteristics are length of the principle void axis, degree of void curvature, and regularity of these features. Brewer (1964) described a void classification based on relative smoothness of void walls on a microscale.

Two void classes based on microscale surface smoothness are orthovoids and metavoids. Orthovoids are "voids whose walls appear morphologically to be due to the unaltered, normal, random packing of plasma and skeleton grains" (Brewer, 1964). "Plasma" represents relatively mobile and unstable solid constituents of soil, while "skeleton grains" represent relatively stable and immobile soil matrix. Metavoids have smoother sides than orthovoids. Under pressure, slicken-sided metavoid walls show evidence of differential movement of parallel planar surfaces (Brewer, 1964). In general, the larger the void, the smoother the void wall. Consequently, the void walls of an ultra microvoid (such as those within soil aggregates) would generally be classified as orthovoids. Macrovoids are generally metavoids due to their relatively smooth walls.

Void arrangements refer to distribution and orientation of individual voids. Distribution of voids in relation to the basic soil aggregate or ped has been divided into intrapedal (voids within peds), interpedal (voids between peds), and transpedal (voids that traverse the soil material without specific associations with individual peds) (Brewer, 1964). Further distribution classification can be based on void groupings such as random, banded, and clustered. Orientation of the voids can be classified as parallel or one of several branching patterns (Brewer, 1964).

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* Optimum moisture refers to the water content of a given soil for which a given compactive effort will yield the maximum bulk density.

Morphologically, Brewer (1964), divided voids into packing voids, vughs, vesicles, channels, chambers, and planes. Packing voids are due to random packing of the individual soil particles. Vughs are larger than packing voids, irregular in shape, and may be interconnected. Vesicles are different from vughs in that they are regular and smooth-walled. Channels are large and roughly cylindrical in shape with smooth walls and a fairly uniform crossection. Chambers are different from vughs in their smooth and regular walls and different from vesicles and vughs due to the interconnection of the chambers by channels. Planes are simply planar voids that are further divided into joint planes (traverse the soil in regular patterns and series), skew planes (traverse soil in an irregular manner with no identifiable pattern), and craze planes (planar voids with a highly complex network of interconnecting short, fat, and curved planes).

Clay minerals have been implicated in at least two types of void formation (Brewer, 1964). Orthovughs are large voids that tend to form in soils with wide particle size distributions. Formation of these voids occur when conditions exist for flocculation of clay minerals present on surfaces of skeletal grains. Should these orthovughs be interconnected, permeability of the soil would increase dramatically. Clay minerals are also responsible for the formation of systems of cracks and planes from shrinking and swelling that accompanies changes in water content.

As voids are essential to understanding pore space in soils, cutans are essential to understanding voids. Cutans have been defined as "a modification of the texture, structure or fabric at natural surfaces in soil material due to concentration of particular soil constituents or in situ modification of the plasma; cutans can be composed of any of the component substances of the soil material" (Brewer, 1964). In other words, cutans are coatings on the soil skeleton that actually form the wall surfaces of soil voids.

Cutans have been classified according to the kind of surface they coat, the nature of the cutanic or coating material, and spacial arrangement or fabric within the cutanic material (Brewer, 1964). Cutans classified according to the surface with which they are associated include grain cutans (associated with skeletal grain surfaces), ped cutans (associated with ped or aggregate surfaces), channel cutans (associated with channel surfaces), and plane cutans (associated with planar void surfaces) (Brewer, 1964).

Cutans have also been classified according to the mineralogy of the cutanic material. Argillans (cutans composed primarily of clay minerals) are the most significant cutan in compacted clay soils. A further subdivision of argillans can be made based on the following criteria: kind of clay mineral, size and shape of clay mineral particles, coating thickness, and contaminants adsorbed to the clay minerals (Brewer, 1964). Two important argillans subdivided according to contaminants associated with the clay minerals are ferri-argillans (clay minerals mixed with iron oxides or hydroxides) and organo-argillans (clay minerals stained with organic compounds).

Clay minerals are probably the most dynamic cutanic materials due to their ability to go into suspensions and readily undergo reorientations (Brewer, 1964). Strong orientation of the plasma associated with a cutan is indicative of its being formed from migrating clay minerals. Furthermore, the voids formed from clay illuviation (migration) tend to be associated with water-conducting voids.

Solid Components

Solid components that dominate behavior of clay soils are organic matter, clay minerals, and cations adsorbed to clay minerals. Organic matter generally imparts structure to clay soil and results in larger pores and higher permeability (Brady, 1974). Low permeability usually associated with clay soils, however, is due largely to characteristics of clay minerals and associated cations.

Native Organic Matter

Soil organic matter consists of partially decomposed plant and animal residues and humus. The residues consist of approximately 60% carbohydrates (sugars, starches, hemicellulose, and cellulose); 25% lignins (exceedingly complex, waxy, resinous material); 5% fats, waxes and tannins; and 10% protein (Brady, 1974). Gieseking (1975) edited a recent text that contained chapters devoted to the following native soil organic constituents: saccharides, nitrogenous substances, organic phosphorous compounds, organic sulfur compounds, fats, waxes, resins, and humic substances. Humus has been defined as "a complex and rather resistant mixture of brown and dark brown amorphous and colloidal substances modified from the original (plant and animal) tissues or synthesized by the various soil organisms" (Brady, 1974). By far the most active part of soil organic matter, as far as its impact on physical and chemical properties of soil, is the colloidal humus fraction. Humus is composed of negatively charged colloids with surface areas and cation exchange capacities far exceeding even smectitic clays (Brady, 1974). Negative charges of humus are highly pH dependent (greater CEC at higher pH). These charges arise from the carboxylic acid and phenolic groups that are abundant on humic substances.

Through interactions with the clay fraction of soil, humus and other organic constituents are largely responsible for formation and stability of soil aggregates. Clays have been shown to interact with many soil organic constituents such as humus (fulvic acid, humic acid, humin, and hymatomelanic acid), proteins, organo-phosphorous compounds, cellulose, hemicellulose, and others (Kononova, 1975).

For centuries it has been understood that soil organic constituents impart to soil a highly aggregated, porous, and structurally stable character. Clay soils with normally low permeabilities can be transformed into highly pervious soils by the addition of organic matter. Thus, in an effort to simulate the action of humus on structure and permeability of clay soils, several synthetic "soil conditioners" have been developed. Examples of these organic compounds are polyvinyl acetate, polyvinyl alcohol, polyacrylamide, polyethylene glycol copolymer, styrene-acrylic acid ester polymers, and many others (Schamp et al., 1975).

It is interesting to note the similarity between some commonly disposed industrial organic sludges and the commercially available soil conditioners (Table 2). It has been a common understanding among farmers the world over that adding organic constituents to poorly drained clay soils can greatly enhance soil structure and drainage properties. The Chinese have for centuries added organic human wastes to improve the soil structure of farmland. Recently, hazardous waste land treatment facilities have found that adding organic sludge to clay soils tends to transform the clay into a highly aggregated and very porous bed. While organic material imparting structure and porosity to clay soils is advantageous to the operation of hazardous waste land treatment facilities, it may be a bad omen for the long term integrity of clay liners.

Hydrophobic surfaces in clay soils are usually formed by certain fractions of native organic matter coating clay surfaces (Letey et al., 1975; Letey et al., 1962). These "water repellent" soils generally have decreased permeability to water but increased permeability to organic fluids.

Clay Minerals

Clay minerals are composed of repeating plate-like structures of SiO_2-tetrahedral and Al_2O_3-octahedral lattice sheets. Two basic combinations of these lattice sheets are represented in 2:1 clays, which consist of one octahedral sheet sandwiched between two tetrahedral sheets; and 1:1 clays, which consist of one octahedral and one tetrahedral sheet. Further differentiation of clay minerals are made on the basis of the degree to which adjacent repeating layers are expandable or by the geometric shape taken by individual clay particles. Table 4 lists the relative sizes and values for several properties of 2:1 and 1:1 clay minerals.

In native clay soils and subsoils, the clay mineral fraction is usually of mixed mineralogical composition. Several clay mineral species are normally present with one or two species dominating. In the following two sections, four of the most widespread clay mineral species are discussed.

TABLE 4. TYPICAL PROPERTIES OF THE 2:1 and 1:1 LATTICE CLAY MINERALS*

Mineral Name and Lattice Description	Unit Particle Thickness			Specific Surface Area (m^2/gm)	Exchange Capacity meq/100gm	Unit Particle Size t=thickness L=length	Particle Shape
	Contracted (nm)	Hydrated (nm)	Potential Volume Change				
Smectite (Expandable 2:1 lattice)	2.0	6.0	200%	800	100	$t = \frac{1}{100} L$	Platy
Illite (Non-expandable 2:1 lattice	20.0	22.0	10%	80	10-40	$t = \frac{1}{10} L$	Platy
Kaolinite (Non-expandable 1:1 lattice	200.0	202.0	1%	8	3	$t = \frac{1}{3} L$	Platy
Halloysite (Expandable 1:1 lattice	70 nm(outside diameter 40 nm(inside diameter) 500 nm(length)			40	12	$t = \frac{1}{7} L$ (where t = outside diameter)	Hollow tubes

*From: Grim (1968); Lambe and Whitman (1979); Theng (1974).

These are 2:1 expandable layer smectites, 2:1 non-expandable layer illites, 1:1 non-expandable layer kaolinites, and multiple form 1:1 halloysites.

2:1 Clay Minerals

Clay minerals with 2:1 lattice configurations include the smectitic and illitic clays. These clays have identical structures except for the bonding mechanisms between adjacent repeating layers. Smectite layers are only loosely bound resulting in a clay with large capacity for volume changes. Illite layers are tightly bound by interlayer potassium ions resulting in a clay with little potential for volume changes. Recent reviews of these clay minerals have been edited by Dixon and Weed (1979).

Smectite. Smectitic clays have a large cation exchange capacity (100 meq/100 gm), specific surface area (800 m^3/gm), and potential for volume change (200%) (Table 4). These properties combine to give smectites the potentially lowest and highest permeability values of clay minerals. Low permeability is due to small unit particle size and large capacity for swelling with water adsorption. Smectitic clays derive high permeabilities from their ability to shrink and crack with water loss.

Smectites have large cation exchange capacities due to their large net negative surface charge. The negative charge comes from Fe^{2+} or Mg^{2+} isomorphous substitution for Al^{3+} in the octahedral sheet, or Al^{3+} substitution for Si^{4+} in the tetrahedral sheet. Cations adsorb to interlayer surfaces of the clay to balance the negative charge arising from within the 2:1 lattice structure (Grim, 1968). The isomorphous substitution discussed above is the predominant source of charge on smectites, but there is a small pH dependent, amphoteric charge associated with broken bonds at edges of the clay crystal (Yong and Warkentin, 1975).

Adjacent 2:1 layers of smectitic clays are only loosely bound by interlayer cations. Smectites readily swell in water from hydration of interlayer cations and adsorption of multiple water layers on interlayer surfaces. Table 4 illustrates that when dehydrated, two smectite layers have a thickness of 2 nm. Hydrated smectites can, however, swell to over 200% of this thickness by adsorbing four layers of water on each of the four available interlayer surfaces.

Clay soils high in smectitic clays usually have very low permeabilities when fully hydrated. However, these soils tend to develop deep and wide cracks when dehydrated (Baver, *et al.*, 1972). Anything that could cause a loss of water from a compacted smectitic clay liner could cause shrinkage cracks to form. These cracks would cause permeability of the clay liner to increase several orders of magnitude.

Extraction of interlayer water has been cited as the cause of shrinking and cracking in smectitic clay soils (Baver, *et al.*, 1972; Grim, 1968). Shrinkage due to removal of interlayer water assumes a decrease in thickness of the water film surrounding individual smectite particles.

However, soil smectites between suction values of zero to 1.36×10^5 mm Hg are assumed to have a constant water film thickness (Emerson, 1962). Therefore it would seem that bulk shrinkage of smectitic clay soils at high water contents ($0-2.72 \times 10^4$ mm Hg of suction) cannot be totally explained by removal of interlayer water. In a study of the shrinkage characteristics for 59 clay soils at high water contents, water film thinning was discounted and deformation of pores was assumed responsible for the shrinkage observed (Greene-Kelly, 1974). Since clay liners are usually kept moist (if not saturated) in the landfill environment, any significant degree of shrinkage would probably involve a more compact repacking of soil particles accompanied by changes in the pore size distribution.

Thickness of the water layer between adjacent smectite lattice sheets affects plasticity, interparticle bonding, compaction, and water movement within clays. These properties change as thickness of interlayer water changes (Yong and Warkentin, 1975). Examination of forces holding water to interlayer surfaces in smectites will assist in predicting the effects of an intruding organic leachate on interlayer spacing in clay liners. It is widely believed that water layers immediately adjacent to smectitic clay surfaces are non-liquid, hexagonally structured, and held more strongly than water layers further out from the surface (Grim, 1968). Thickness of this structured water varies depending on the adsorbed cation. Smectites have a structured water thickness of 1 nm or four water layers per clay surface when calcium is the adsorbed cation. Sodium smectite has a structured water thickness of 0.75 nm or 3 water layers on its surfaces (Grim and Cuthbert, 1945). Glaeser (1949) found, however, that the distance between dehydrated smectite layers exposed to acetone increased to 1.25 nm and 1.51 nm when sodium and calcium, respectively, were the adsorbed cations. Thus, properties of smectites vary greatly depending on the distribution of exchangeable cations (Yong and Warkentin, 1975).

Surface-bound layers of water are held strongly to the clay. However, they represent only part of interlayer water. Water layers further out from clay surfaces are held in place by hydrogen bonding, forming chains extending back to structured water layers anchored to the clay surface. These outer layers of water can more easily be displaced by an intruding fluid. Smectitic clays have been shown to interact with nitriles, esters, and ethers (Hoffman and Brindley, 1960), organic bases (Theng, et al., 1967; Cloos et al., 1979), aromatic compounds (Greene-Kelly, 1955), alcohols (Annabi-Bergaya et al., 1979), surfactants (Brindley and Rustom, 1958), polyvinyl alcohol (Greenland, 1963), ketones (Parfitt and Mortland, 1968), glycols and glycerols (Hoffman and Brindley, 1961), and several polyfunctional organic liquids (Bradley, 1945). Several good reviews of these interactions have been published (Theng, 1974; Mortland, 1970).

Smectites readily adsorb polar and positively charged organic species on interlayer surfaces. Since smectitic clays can swell in water to 200% of their dehydrated volume, large amounts of shrinkage can occur if interlayer water is displaced by other fluids which yield a lower interlayer spacing.

Interlayer spacing in smectitic clays increases as the dielectric constant and dipole moment of the adsorbed fluid increase (Barshad, 1952; Grim, 1968). Since water has both a very high dielectric constant and dipole moment, its replacement in clay interlayer spaces by most polar organic solvents would cause significant decreases in interlayer spacing. Interlayer shrinkage, even just along large pore walls, could cause significant increases in permeability of a clay liner.

Illite. Illite is a field term loosely defined as clay-sized micaceous minerals. These clays have specific surface area (80 m^2/gm), cation exchange capacity (10-40 meq/100 gm), and potential for volume change (10%) intermediate between smectite and kaolinite. Illite also has intermediate particle thickness relative to the other clays listed in Table 4. As with smectites, the source of charge in illitic clays is isomorphic substitution in the clay lattice and to a lesser degree the pH dependent charges on broken bonds at edges of the clay crystal (Yong and Warkentin, 1975).

Many illitic soils are actually admixtures of interstratified structures of illite, smectite, and vermiculite (Theng, 1979). Hence, there is wide variation in composition and physiochemical properties associated with this clay mineral.

Adjacent illite layers are tightly bound by interlayer potassium cations fixed between repeating 2:1 layers. Consequently, this non-expandable clay usually will not adsorb water or polar organic fluids on interlayer surfaces. This interlayer exclusion causes illite to have potential for no more than 10% shrinkage or swelling. However, MacIntosh et al. (1971) found that an organic cation that closely approximates the size and charge of potassium (such as dodecylammonium) could replace this cation in the interlayer. Except in the rare case stated above, adsorption of organic chemicals will largely be confined to external unit particle surfaces.

Illite-silt mixtures have been shown to undergo decreases in permeability with decreasing electrolyte concentration followed by permeability increases if the electrolyte concentrations were subsequently increased (Hardcastle and Mitchell, 1974). The permeability increase appeared to the authors to be due to a slight decrease in clay swelling.

Illitic clays have been shown to interact with organic bases (MacIntosh et al., 1971), organic acids and peptides (Greenland et al., 1965), organic polymers (Schamp et al., 1975), glycol (Parfitt and Greenland, 1970), alcohols (Greenland, 1972), and proteins (Albert and Harter, 1973). Recent reviews are available that summarize the literature dealing with illite interactions with low molecular weight organics (Theng, 1974) and organic polymers (Theng, 1979).

1:1 Clay Minerals

Kaolinite is both a general term for 1:1 layer clay minerals and a specific term for 1:1 non-expandable clays. Another member of the 1:1 clays is halloysite which has hydrated interlayers and is shaped like hollow tubes. There appears to be continuous gradations between these two

1:1 clay minerals (Carroll, 1970; Theng, 1979). These clays obtain their exchange capacity both from pH dependent charges on broken bonds at edges of the clay crystal and ionization of hydroxyl groups on basal surfaces of the clay (Yong and Warkentin, 1975). A general review of these clay minerals has been written by Dixon (1979).

Kaolinite (Species). Kaolinitic clay has low cation exchange capacity (3 meq/100 gm), specific surface area (8 m^2/gm), and only small potential for volume change (Table 4). Adjacent 1:1 layers are tightly bound by a network of hydrogen bonds that usually prevents interlayer penetration of fluids (Grim, 1968). The 1:1 layers are stacked into hexagonal platelets ranging in thickness from 0.05 to 2.0 m. Except where the interlayer space has been expanded by certain inorganic salts (Wada, 1961), organic fluids only adsorb to external surfaces of the hexagonal platelets.

Kaolinite has been shown to interact with organic bases (Grim *et al.*, 1947), amines (Conley and Lloyd, 1971), polyvinyl alcohols (Greenland, 1972), organic acids (Evans and Russell, 1959), polymers (Sakaguchi and Nagase, 1966), alcohols (German and Harding, 1969), and various other polar organic compounds (Olejnik *et al.*, 1970). Loeppert *et al.* (1979) investigated the influence of basic, polar, and nonpolar organic fluids on the acidic crystalline edge sites of kaolinite. The influence of polar and nonpolar organic fluids on permeability of compacted kaolinite was investigated by Michaels and Lin (1954). They found that changing from water to a nonpolar organic fluid could cause significant permeability increases.

Halloysite. Halloysitic clays are similar in composition to kaolinite with the exception of interlayer bonding and geometric configuration. Instead of hydrogen bonding between adjacent layers, halloysite often has a tubular geometric configuration when viewed in the dehydrated state by electron microscopy (Theng, 1979). Hydrated halloysite has a larger specific surface area (40 m^2/gm) and cation exchange capacity (12 meq/gm) than kaolinite.

Halloysite has been shown to interact with a variety of organic compounds (Carr and Chih, 1971) such as glycols, ethers, alcohols, amines, ketones, aldehydes, nitriles, nitroso-compounds (MacEwan, 1948; MacEwan, 1949), and amides (Weiss and Russow, 1963). While the kaolinitic species generally do not permit interlayer penetration of water or organic fluids, halloysitic species readily adsorb polar and basic organic fluids on interlayer surfaces (MacEwan, 1948).

Another noteworthy property of halloysite is its amphoteric nature. That is, halloysite may exhibit either positive or negative charges depending on the pH. One side of halloysite has a network of hexagonally arranged oxygens, whereas the other side is a network of hydroxides (Theng, 1979). Geometrically, halloysite graduates from slightly curved hexagonal platelets (hydrated) to individual 1:1 layers tightly curled into tubular structures (dehydrated) (Table 4).

Halloysite exists in nature in both hydrated and dehydrated forms. It is hydrated forms that readily adsorb polar fluids and organic cations on interlayer surfaces. However, if water of hydration is lost due to heating or extraction, the clay takes on the curled tube shape. Once this form of halloysite (referred to as metahalloysite) is dehydrated, it will not readily rehydrate and loses its capacity for adsoption of polar organic fluids (MacEwan, 1948).

Exchangeable Cations

Exchangeable cations are positively charged ions that are reversibly adsorbed to negatively charged clay surfaces (Brady, 1974). Both the composition of exchangeable cations and resulting equilibrium concentration of the cations in soil water will greatly affect the permeability of a compacted clay soil (Marshall, 1959).

Effects of composition of exchangeable cations on permeability of smectite, illite, and kaolinite are illustrated in Fig. 7. In general, a clay saturated with divalent cations (such as calcium) is more permeable than one saturated with monovalent cations such as sodium (Yong and Warkentin, 1975).

Sodium has a large hydrated radius which results in large interlayer spacing and hence disperses the clay. The dispersed clay particles are free to migrate with the percolating leachate, eventually lodging in and clogging pores, effectively reducing permeability. However, if there were higher salt concentration in a clay than free water to hydrate the salts, the effective hydrated radius of sodium and interlayer spacing between the clay particles would decrease. Thus, while sodium-saturated clay will generally have low permeability, if the concentration of salts in the soil were large enough, the clay might not disperse. Without the dispersed clay clogging pores, soils with excess salts almost always exhibit permeabilities larger than a soil saturated with sodium but with lower overall salt content (Quirk and Schofield, 1955).

Calcium has a relatively small hydrated radius and two charges per atom. These characteristics combine to make calcium-saturated clay soils more resistent to dispersion and generally more permeable than sodium-saturated clay soils (Yong and Warkentin, 1975).

While the trend toward lower permeabilities with increasing exchangeable sodium levels is same for all clays, the effect is more pronounced for smectitic clays (Fig. 7). This is due to the relatively large cation exchange capacity, specific surface area, and hence capacity to swell of smectite. Sodium-saturated smectite adsorbs interlayer water to yield basal spacing from 1 nm (oven dry state) to over 5 nm (Theng, 1979). This represents a thickness of 4 nm for water on each surface. While this much interlayer expansion would at first appear advantageous for reducing clay liner permeability, the expansion is reversible and hence sodium smectite is susceptible to shrinkage. Another problem with sodium smectite is that when fully expanded, it is susceptible to dispersion and internal erosion. When a clay is dispersed, it lacks structural strength and will flow as a

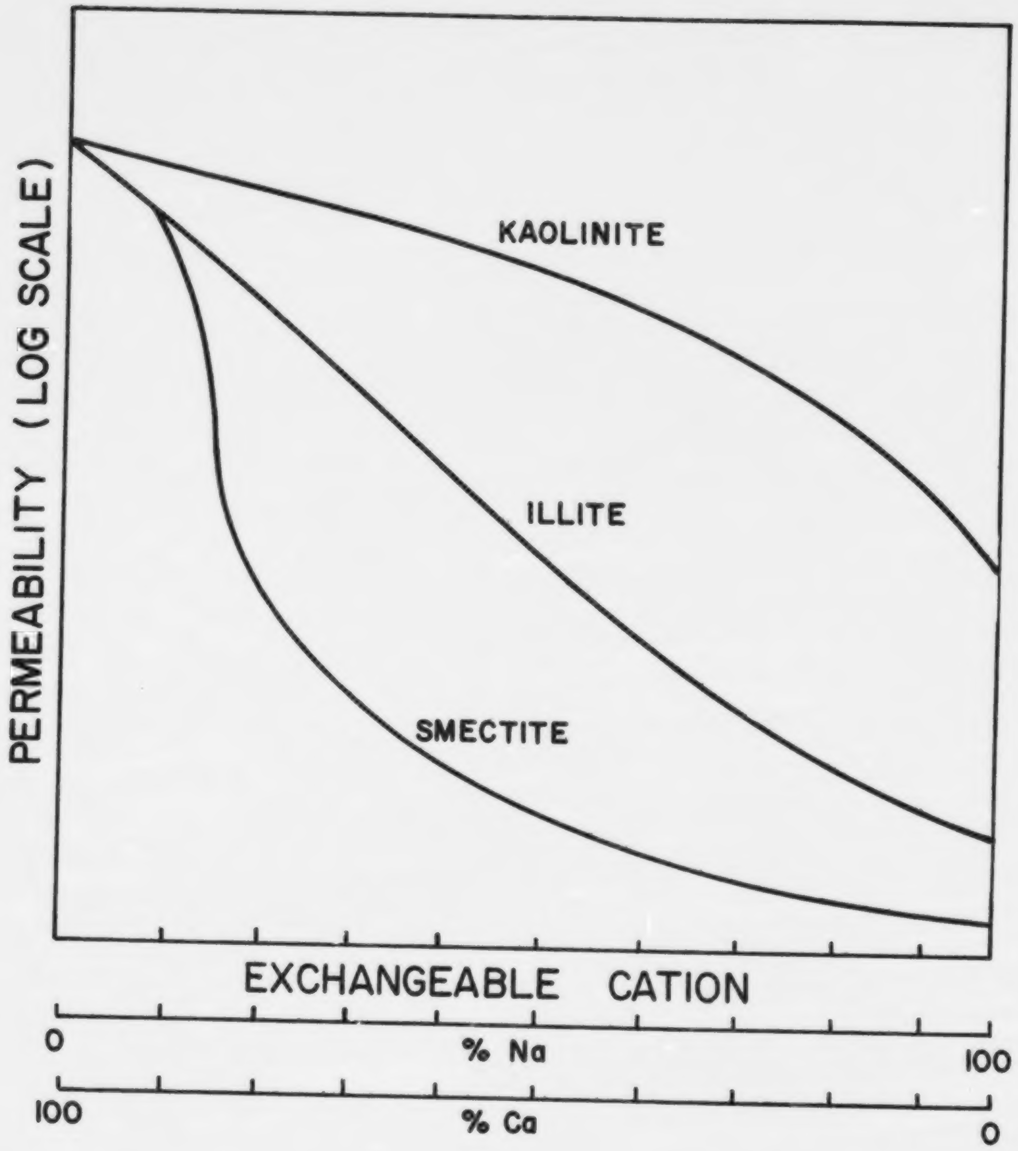

FIG. 7 Effect of the Composition of Cations on the Permeability of Clays (Modified from Yong and Warkentin, 1975)

viscous fluid. This may cause problems such as loss of strength in waste impoundment sidewalls.

Calcium-saturated smectite adsorbs interlayer water to yield stepwise increases in basal spacing from 1 nm (oven dry state) to about 2 nm (Theng, 1979). This corresponds to a 1 nm thickness of water per surface when Ca-smectite is fully expanded. With divalent cations such as calcium or magnesium adsorbed to surfaces, the clay is resistant to swelling and dispersion. Clay in a calcium-saturated state tends to be flocculated into stable aggregates of 10 or more clay particles. These aggregates act as larger unit particles and thus pores between these unit particles tend to be larger than pores in a dispersed clay. Formation of these interaggregate macropores is the primary reason for larger permeability of a divalent cation-saturated clay.

Waldron and Constantin (1968) found that permeability of sodium-saturated smectites decreased when NaCl concentration in the percolating leachate decreased. A similar clay saturated with calcium showed no appreciable decrease in permeability with respect to decrease in calcium concentration in the leachate. Quirk and Schofield (1955) similarly showed larger permeability decrease with decreasing leachate salt concentration for clays with higher exchangeable sodium percentages. Hughes (1975) examined the effect of a concentrated salt solution (water containing 3.1% NaCl + 3.6% Na_2SO_4) on permeability of a clay liner constructed from a mixture of sandy soil and sodium-saturated smectite. With a four foot head of water, permeability of the clay liner increased 100 fold (from 1.0×10^{-6} to 1.0×10^{-4} cm/sec) in seven days.

McNeal (1968) developed a procedure for predicting permeability of soils containing swelling clays. For smectites in mixed salt solutions for a given SAR sodium adsorption ratios (SAR = Na/(Ca + Mg) , where amount of adsorbed cations is given in mmole/liter), permeability was always found to be greater at lower SAR values. At given SAR values, the permeability decreased with decreasing salt concentration of the percolating leachate.

McNeal and Coleman (1966) evaluated the effect of decreasing followed by increasing electrolyte (salt) concentration of soils with smectitic, illitic, and kaolinitic clay fractions. They found that permeability of soils rich in kaolinitic clays were relatively insensitive to decreases or increases in salt concentration. Soils with predominantly illitic clays showed moderate decreases in permeability with decreasing salt concentration and no change in permeability with increasing salt concentration. Smectitic clays showed large permeability decreases with decreasing salt concentration, and only soils with a large amount of smectitic clays showed any recovery of initial permeability values with increasing salt concentrations.

FAILURE MECHANISMS OF CLAY LINERS

Failure mechanisms of clay liners are defined here as any interaction of the compacted clay soil liner that can substantially increase its permeability. Climatological cycles (wet-dry, freeze-thaw, percolating rainfall that dissolves soluble clay soil components, etc.) are widely understood to be responsible for much of the structural development and permeability increases in clay soils (Brewer, 1964; Brady, 1974). However, this text is mainly devoted to investigating a much less understood context of structural development in clay soils: the inservice environment of a remolded and compacted clay soil liner used for hazardous waste landfills and surface impoundments. Two main failure mechanisms discussed are dissolution and piping, and volume changes.

Dissolution and Piping

Dissolution and piping are considered together because their effects on permeability of a clay liner tend to be complimentary. As a dissolving agent erodes pore walls, the released fragments of soil tend to clog pores unless these particle fragments are "piped" out of the compacted clay soil. Theoretical investigations of clogging have been reviewed by Kovacs (1981).

Both organic and inorganic acids and bases react with, and many dissolve, portions of compacted clay soils. Acids dissolve aluminum, iron, and silica, eroding the lattice structure of clays and releasing undissolved fragments for migration with a percolating leachate (Grim, 1953). Acids may also oxidize native organic matter and dissolve calcium carbonate nodules.

Solubility of silica is affected by a variety of environmental factors and the form of silica. Amorphous silica is more soluble than crystalline or polymeric silica. Silica is more soluble at higher temperatures, pressures, and pH's (Yariv and Cross, 1979). Of course, larger particles of silica-containing minerals will be slower to solubilize due to decreased surface area. Wey and Siffert (1961) showed that aluminum and magnesium ions drastically affect solubility of silica in pH ranges of 5 to 10.5 and 10 to 12 respectively.

Silica is also more soluble in the presence of organic acids such as those found in humic acids (Barnum *et al.*, 1973; Bartels, 1964). Bases have been shown to extract silica from clay lattice structures (Nutting, 1943). Solubility of silica is pH dependent and greatly increases above pH 9 (Alexander *et al.*, 1954). Amorphous silica is more soluble than crystalline or polymeric silica, but exact solubility measurements are difficult due to slowness of equilibria and large solubility effects (Krauskopf, 1956).

Usually pore sizes present in compacted clay soils are not large enough to transport slaked fragments produced by reactive acids or bases. In this case, pore clogging and at least a temporary decrease in permeability of a clay liner would occur. If, however, the clay liner were placed atop stratum containing pores large enough to "pipe" soil fragments or if

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clogging fragments themselves were dissolved, permeability increases could eventually be expected to occur.

Piping has been described as "active erosion of soil from below the ground surface which occurs as a result of substratum pressure and the concentration of seepage in localized channels" (Mansur and Kauffman, 1956). Jones (1978) found early stages of piping development to be associated with vertical contrasts in structure and permeability of soils. Soil piping was also associated with shifts in soil pore size distribution toward macropores with no corresponding change in total porosity. A reactive fluid may enlarge surface area of pores by dissolution of the soil matrix between two pores. While reactivity in a fluid is reduced by its action on the pore wall, the size increase in the pore will increase rate of delivery of the fluid to the pore. In this manner, any variability in pore size distribution of a clay liner may be magnified with time. Schechter and Gidley (1969) found that wormhole formation was the result of a reactive fluid preferentially flowing in larger pores. They further found that quasi-equilibrium was reached where further growth of a pore was limited by the rate of diffusion of the reactive fluid.

Mitchell (1975) found that quick clays were often associated with the presence of organic compounds possessing strong dispersing characteristics. These clays act as viscous fluids with no structural strength and are thus susceptible to erosion caused by seepage. Reservoir water seeping into earthen dams has been reported to cause dispersive piping and eventual tunneling all the way through the dams. Tunneling was reported to occur in soils with a local permeability of greater than 1×10^{-5} cm/sec.

Similarly, differential solution and subsequent leaching has been reported to result in formation of channels, sink holes, and cavities (Mitchell, 1975). This was found to be especially true with calcareous sediments. Cedergren (1967) reported that differential leaching of limestone, gypsum, and other water soluble mineral components could lead to development of solution channels that increase in size with time and substantially increase permeability.

It is important not to underestimate the importance of minor soil and geologic detail on permeability of soil formations. Cedergren (1967) found that such minor details caused the majority of failures in dams, reservoirs, and other hydraulic structures. Furthermore, he concluded that most failures caused by seepage could be placed in the following two categories:

1. Those caused by soil particles migrating to an escape exit resulting in piping and erosional failures;

2. Those caused by uncontrolled seepage patterns leading to saturation, internal erosion, and excessive seepage.

Crouch (1978) found that tunnels and tunnel-gullies (or pseudokarsts) developed in dispersive soils where soil-colloid bond strengths were low compared to energy of water flowing through the soil. He found that dispersive soils or those with low structural stability were associated with tunnel erosion throughout the world. Other factors found to be related to tunnel erosion were Exchangeable Sodium Potential (ESP), soil cracks, low permeability, and hydraulic gradients.

In a study of variables affecting piping, Landau and Altschaeffl (1977) noted strong interaction between chemical composition of eroding water and compaction water content. Ion concentration seemed to have little effect on soil piping susceptibility for mixed illitic and kaolinitic clay loam compacted dry of optimum. For the same soil compacted wet of optimum, soil piping susceptibility was highly related to ion concentration in eroding water. The authors suggested that wet of optimum compaction produced more parallel orientation of soil particles which increased the effect of osmotic repulsion. Consequently the ion concentration of soil water would have a relatively greater effect on dispersive forces in soil compacted wet of optimum. When low ion concentration eroding water was combined with wet of optimum compaction, they reported an exceptionally low resistence to internal erosion. These findings are felt to be especially important due to the long standing practice of compacting clay liners wet of optimum to produce minimum initial permeability possible for a given compactive effort.

Piping involves slaking soil particles. Slaking is defined as disintegration of unconfined soil samples when submerged in a fluid. Moriwaki and Mitchell (1977) investigated dispersive slaking of sodium and calcium-saturated kaolinite, illite, and smectite. All the clays slaked by dispersion when saturated with sodium, with the process proceeding faster with sodium kaolinite and sodium illite. Sodium illite swelled slightly, while dispersion of sodium smectite was preceded by extensive swelling. Sodium kaolinite underwent no visible swelling while dispersing. For calcium-saturated clays, illite dispersed much more slowly while the rate of dispersion increased for kaolinite and smectite. Calcium kaolinite was thought to disperse faster because of its higher permeability relative to sodium kaolinite. Sodium smectite was thought to disperse slowly because of the large degree of swelling it underwent. This would lower permeability, thus slowing water entry and retarding dispersion.

Compaction has been shown to decrease the electrolyte content of expelled interlayer water (Rosenbaum, 1976). Such lowering of fluid electrolyte concentrations in sodium-saturated clays may cause substantial swelling and dispersion (Hardcastle and Mitchell, 1974). This dispersion causes particle migrations. If there were fluid-conducting pores large enough to transport these dispersed clay particles, permeability increases and soil piping might result (Aitchison and Wood, 1965). It is important to note that piping would initiate on the underside of a clay liner where clay particles can migrate into substrata containing larger pore diameters. The soil pipe would then progress upward through the clay liner until it found an opening into the impoundment. Since clay particles have been shown to migrate through porous media containing less than 15% clay (Hardcastle and Mitchell, 1974), clay liners underlain by soils containing less than 15% clay may be susceptible to soil piping.

Four laboratory tests for the determination of soil susceptibility to dispersive erosion have been developed by the U. S. Soil Conservation Service. A major conclusion of a recent symposium on soil piping was that these four tests should be performed on soils where piping can cause unacceptable damage (Sherard and Decker, 1977). The four tests (ASTM Special Technical Publication Number 623) are the pinhole test, a test of dissolved salts in pore water, the SCS dispersion test, and the crumb test. Ideally, the tests should incorporate both primary and secondary waste leachates.

Volume Changes

Volume changes occur in clay soils from bulk and interlayer shrinkage. Bulk shrinkages are usually identifiable by visual inspection of a clay liner. This type of shrinkage is represented by macrostructural features such as cracks, fissures, joints, faults, slickensides, shears, channels, ice wedges, planes, and chambers. Interlayer shrinkages may not be detected by visual inspection, but their impact on permeability of a clay liner can be just as dramatic. This type of shrinkage is represented by microstructural alterations in the clay liner which are usually manifested as shifts in pore size distribution. An extensive review of voids in soil that result from bulk and interlamellar shrinkage has been written by Brewer (1964).

Volume changes in clay liners occur when there is a change in water content of clay. Adsorption of water on exposed surfaces occurs with all clay minerals, with the exception of completely dehydrated halloysite. For a given change in water content, the magnitude of volume change is dependent on clay mineral type, arrangement of clay particles, size of clay particles, surface area per unit weight of clay, and kind and proportion of cations adsorbed to clay. Smectite, and to a lesser degree illite, may cause problems associated with changes in volume of clay liners (Table 4).

Two contracted lattice sheets of smectitic clays have a 2 nm thickness. Since each layer of adsorbed water is approximately 0.25 nm thick, the adsorption of four water layers on each of the two external and interlayer surfaces would give a smectitic unit particle (2 clay layers) an increase in volume of 200% between the dehydrated and hydrated states. It is the small size and expandable lattice properties of the smectitic unit particle that give this clay its uniquely large potential for volume change (Theng, 1979).

Extraction of interlayer water causes shrinking and associated cracking exhibited by smectitic soils (Baver, et al.,1972; Grim, 1968). Cracking is a result of the clay undergoing three dimensional shrinkage. Where the rate of water extraction is not uniform, cracks will form in wetter soil (Yong and Warkentin, 1975). Water content of a clay liner may change if an organic leachate extracts water from the clay liner.

Shrink-Swell Behavior

Swelling behavior of compacted clay soils has been shown to be related to clay minerals present (Yong and Warkentin, 1975), presence of organic compounds adsorbed to clay surfaces (Hughes, 1975; Barrier, 1978), exchangeable cations present (Norrish, 1954), fabric or structural arrangement of clay particles (Lambe, 1958a, 1958b), overburden pressure (Davidson and Page, 1956), and Atterberg limit values of clay soils (Holtz and Gibbs, 1956). Swelling tends to decrease permeability of clay soils, but simultaneously indicates potential for shrinkage should the soil environment be altered substantially.

Swelling behavior of clays is significantly affected by the clay minerals present (Table 4). Both kaolinite and illite have substantially less capacity to swell than smectitic clays. Halloysite has a shrink-swell potential between that of kaolinite and illite.

Smectite owes its large shrink-swell capacity to a combination of its large cation exchange capacity, moderate surface charge density, octahedral layer isomorphous substitution, and large surface area to volume ratio (Gast, 1979). With larger population of exchangeable cations, there will be a correspondingly larger potential volumetric increase upon hydration of the cations. A moderate surface charge density leaves more clay surface area for water adsorption and allows more water of hydration to be positioned between the cation and the clay surface.

In smectites, the octahedral lattice sheet is sandwiched between two tetrahedral lattice sheets, and most isomorphous substitution occurs in the octahedral sheet. That is, substitution of Mg^{2+} or Fe^{2+} in the octahedral lattice positions normally held by Al^{3+} gives smectitic clays a net negative charge. Furthermore, since the negative charge emanates from the middle of the lattice structure, the electrical charge is diffused or evenly spread over the entire clay surface. The diffuse nature of the negative charge plus the relatively small charge density of smectites decrease the rigidity with which exchangeable positively charged cations are held to the clay surface. This permits formation of a wide, diffuse, electrical double layer. The repulsive forces between adjacent cation-covered positively charged double layers enable the monovalent saturated smectites to continuously swell until one of the following occurs:

1. Repulsive swelling continues until all remaining attractive forces are overcome, and the clay disperses into individual particles forming a gel, sol, or suspension (Theng, 1979).
2. Confinement pressure of the surrounding clay soil body prevents further swelling (Lambe and Whitman, 1979).
3. Swelling causes a shift in pore size distribution toward larger number of micropores and smaller number of macropores (Lauritzen and Stewart, 1941).

Since smectites have a large surface area to volume ratio which gives the clay approximately 800 m^2/gm available surface to which water can adsorb, this large amount of adsorbed water represents a large potential for shrinkage or swelling (Theng, 1979).

An important aspect of the shrink-swell behavior of kaolinite and illite is that these clays shrink upon dehydration but show very little swelling upon subsequent rewetting (Yong and Warkentin, 1975). This characteristic limits the capacity for these two clays to "self heal" or to close shrinkage cracks once formed.

Smectitic clays have a large and reversible capacity for volume changes under normal conditions. However, Gieseking (1939) found that smectites lose their capacity for "self healing" or swelling when exposed to organic cations. Barrier (1978) reported the swelling of smectites after exposure to neutral polar organics (alcohols, glycols, ketones, and acetonitrile) and neutral nonpolar organics (xylene and cyclopentane). Watson (1968) found that certain concentrations of surfactants stabilize soils against dispersion and swelling, thereby preventing a decrease in permeability of a soil. Hughes (1975) found that one reason for reversal of swelling in smectites was adsorption of organics on clay surfaces. He suggested that adsorbed organics interferred with the interactions between interlayer water and clay surface. Grim (1968) found that water adsorbing properties of smectitic clays were reduced as interlayer spaces were coated by organic cations. He noted that "in general, the larger the organic ion, the greater is the reduction in the water adsorbing capacity." Grim _et al_., (1947) also found that the water adsorption capacity of kaolinitic clays were reduced following treatment with organic cations. The decrease in water adsorption was less than the decrease exhibited by smectitic clays. Grim (1968) assumed that the water adsorption decrease for other clays would be intermediate between those for smectite and kaolinite.

Hughes (1975) found that exchangeable cations could affect the swell behavior of clay soils in at least two ways, as follows:

1. Exchange of monovalent cations for divalent cations could cause reversal of swelling.

2. Presence of excess sodium could compete for available water with clay surfaces causing a decrease in interlayer spacing of the clay.

Norrish (1954) showed initial or crystalline swelling of clays to be directly related to hydration energies of interlayer cations. Crystalline swelling has been defined as the swelling range at which "the gross crystal morphology is preserved" (Theng, 1979). Within this range of water content, swelling pressure exhibited by clay minerals is largely determined by exchangeable cations (Norrish, 1972). Above the water content range of crystalline swelling, the valence of the exchangeable cation controls the swell behavior of smectites.

Monovalent cation-saturated smectites will generally continue to swell beyond the crystalline range into state II or osmotic swelling (swelling due to the migration of water to higher salt concentration in interlayer water as compared to interpedal or interaggregate water). The consistency of smectite in this state ranges from that of a still paste at the low end of water content range ($\sim$0.7 gm H_2O/gm clay), to that of a thick gel at the high end of the scale ($\sim$20 gm H_2O/gm clay) (Theng, 1979).

Soil fabric or structure has been defined as the physical constitution of a soil material as expressed by the spacial arrangement of the clay and other solid particles and associated voids. Of special importance in clay soils are the extremes of possible spacial arrangements of clay particles from the flocculated structure (edge to face) to the dispersed structure (face to face). Clay soils with a dispersed structure will tend to undergo more volumetric shrinkage with changes in water content (Lambe, 1958a). The degree of dispersed structure (parallel orientation) exhibited by compacted clay soils increases as water content of the soil or compaction effort are increased (Fig. 8) (Lambe, 1958b).

Structural form affects permeability as well as swelling behavior of a compacted clay soil (Mitchell and Hooper, 1965). The flocculated structure associated with compaction on the dry side of optimum moisture results in larger average pore diameters and permeabilities than exhibited by clay soils compacted at water contents on the wet side of optimum (Fig. 8). In either case, Mitchell (1975) concluded that compacted clays revert to more flocculated structure after placement and hence may exhibit a several fold increase in permeability with time.

Another factor which influences clay liner swelling and shrinking potential is overburden pressure. Swelling pressure in clays will determine the extent to which it is capable of swelling under a given overburden pressure. Davidson and Page (1956) determined that swelling pressure exhibited by sodium saturated mineral samples of smectite was substantial, while that exhibited by kaolinite and illite was negligible.

Swelling pressure exerted by smectites in the crystalline swelling state ($\sim$0.0-0.1 gm H_2O/gm clay) is approximately 10^9-10^7 dyne/cm^2. The opposing forces generating this net swelling pressure are cation hydration (repulsive) and electrostatic attraction (Norrish, 1972). Hence, swelling pressure in this state is largely determined by hydration energy of the cation, and would be expected to decrease with increasing cation valence. Consequently, smectites saturated with divalent cations do not normally swell past the $\sim$2nm interlayer spacing limit of crystalline swelling (Theng, 1979). In other words, interlayer repulsive force of cation hydration is less than both van der Waals forces of attraction between adjacent clay sheets and electrostatic attractions between divalent cation and negatively charged clay surfaces. Clays saturated with monovalent cations continue to exert a net swelling pressure (10^7-10^5 dyne/cm^2) at interlayer spacings greater than 2nm with water contents from $\sim$0.7-20gm H_2O/gm clay. Net swelling pressure at these interlayer spacings is due to the following two opposing forces:

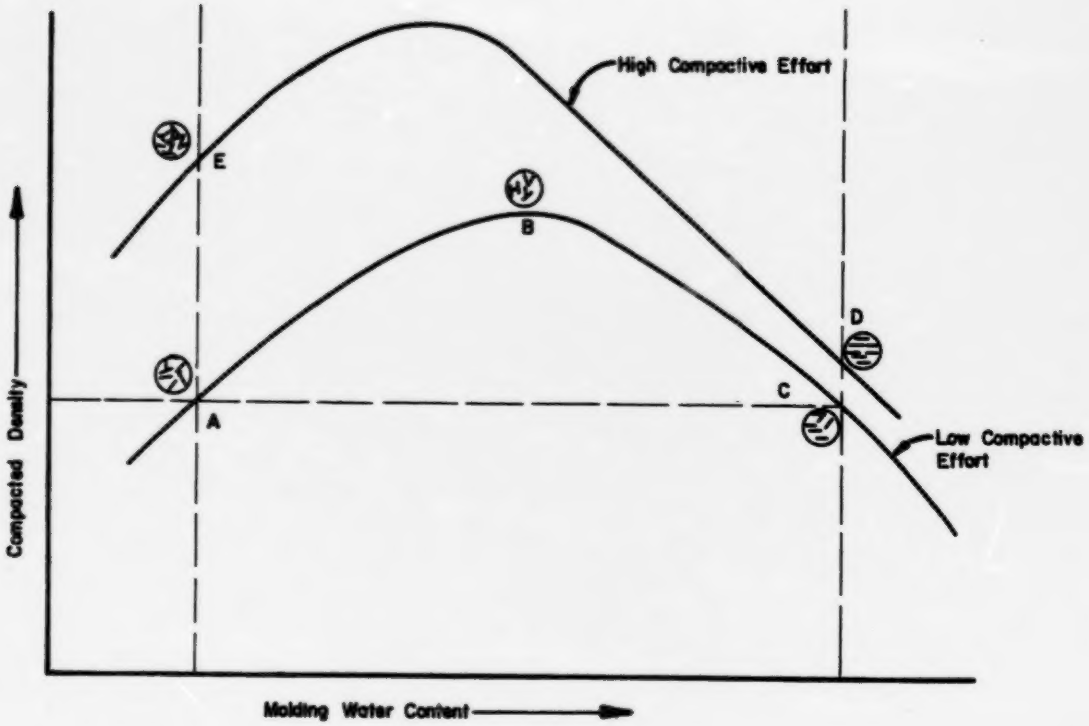


FIG. 8. Effects of Compaction Water Content on the Structural Arrnagement of Clay Minerals (Lambe, 1958b)

1. Repulsive, osmotic forces of interacting diffuse electrical double layers (i.e., mutual repulsion of cation rich hydration shells surrounding adjacent clay sheets);

2. Frictional forces generated by edge to face bonding of the clays and, to a lesser extent, van der Waals attractive forces (Theng, 1979; Norrish, 1972).

Potential for volume changes in a clay also can be significantly related to Atterberg limit values such as the "plastic range" and "shrinkage limit" of the clay (Holtz and Gibbs, 1956). The "plastic range" is the range of water content below which a clay will lose its cohesiveness. The "shrinkage limit" is the water content of a clay below which no further shrinkage is possible. Values for Atterberg limits are given for clays with low, medium, and high swell potential in Table 5.

TABLE 5. SWELL POTENTIAL VERSUS ATTERBERG LIMIT VALUES IN THREE CLAY SOILS*

	Swell Potential		
	Low	Medium	High
Plastic range[1]	<30	30-50	>50
Shrinkage limit[1]	>12	10-12	<10

* After Holtz and Gibbs (1956)

[1] Water content as percentage dry weight

Swelling behavior in clay soils is a complex result of many interacting mechanisms. Bowles (1979) found swell behavior of soils to be related to clay type, overburden pressure, void ratio, method of saturation, and general environmental conditions. Franzmeier and Ross (1968) reviewed factors affecting swell potential of 30 kaolinitic, illitic, and smectitic clay soils. They found swell potential of clay soils to be most significantly related to kind and amount of clay and soil fabric (expressed as amount of clay per unit dry volume of soil).

A recent review of the shrinking and swelling behavior of clay soils has been written by Brown (1979). The review extensively discusses shrink-swell behavior relating to swelling pressure, Atterberg limits, structure, strength, stabilization, water holding capacity, and permeability of clay soils.

Interlayer Spacing Changes

Interlayer spacing of clay minerals refers to spacing between adjacent basal surfaces. This includes the thickness of one clay layer plus the thickness of the sorbed fluid layer between two adjacent clay layers. Changes in interlayer spacing of clay may impact its bulk volume, pore size distribution, and thus permeability. Factors affecting this spacing include the clay mineralogy, properties of the fluid, and the exchangeable cations adsorbed to the clay minerals. A related phenomenum, applicable to all solid surfaces in clay liners, is the change in thickness of the fluid films coating soil particles and lining soil voids.

In the service environment of a compacted clay soil liner, nearly all accessible clay mineral surfaces are water-wet. Two significant exceptions are clay surfaces coated with naturally occurring hydrophobic substances and the fully dehydrated form of halloysite. The following discussion emphasizes interlayer spacing changes that may occur in initially water wet clays or dehydrated clays exposed to water and organic fluids simultaneously.

Effect of Clay Mineralogy. Clay minerals exhibit interlayer spacings that reflect strength of bonding between adjacent clay layers. The non-expandable clay minerals (illite and kaolinite) only rarely undergo interlayer spacing changes due to strength of interlayer bonds. Expandable lattice clays (smectites and to some extent halloysite) have much weaker interlayer bonds and thus are able to intercalate (adsorb between adjacent layers) water and a variety of polar or cationic organic fluids.

Smectites are by far most geographically widespread of the expandable lattice clays. Due to the large hydrated radius of monovalent sodium, smectites saturated with this cation adsorb water until the clay disperses into a clay-water suspension. At this point, the water layers are several times the thickness of the clay layers (Theng, 1979). In the case of divalent cations, interlayer expansion is normally limited to the point where water layers are about equal to the clay layers in thickness (Theng, 1979; Grim, 1968). This is caused by strong electrostatic attractions between negatively charged clay sheets and the two positive charges on the divalent cation (Theng, 1974).

Another property of clay minerals that affects interlayer expansion is interaction between interlayer cations and dipoles present on the clay surface. Cation-dipole interactions have been found to dramatically affect interlayer spacings of homoionic smectites with acetone and ethanol (Bissada et al., 1967). Interlayer spacing increased with cation sequence $K^+ < Na^+ < Ba^{++} < Ca^{++}$ for both acetone and ethanol. Through cation-dipole interactions, divalent cations were found to increase adsorption of organic molecules. For ions with the same valence, the smaller ion caused greater adsorption and hence the largest interlayer spacing. Olejnik et al. (1970) further discuss the effects of cation-dipole interactions, and Theng (1979) describes the "profound influence on the adsorption process" of interlayer cations.

Other clay mineral properties that affect interlayer spacing resulting from exposure to particular organic fluids include surface acidity, surface charge density, tetrahedral/octahedral layer charge ratio, surface coatings, and degree of weathering (Swoboda and Kunze, 1968; Yariv and Heller, 1970; Grim, 1968). Excellent reviews of effects of various factors on interlayer spacing of clay minerals can be found in Theng (1979; 1974), Grim (1968), Yariv and Cross (1979), Mortland (1970), and Yong and Warkentin (1975).

Characteristic interlayer spacings for clay minerals with water as adsorbed fluid are given in Table 6. These values are "typical" and may vary substantially depending on types of exchangeable cations, degree of clay mineral weathering, and previous treatments that the clay has undergone.

Effects of Organic Fluids. Any change in water content of a clay mineral is likely to cause change in interlayer spacing. This can be accomplished by displacing, extracting, or replacing water in either soil pores or interlayer spaces.

Water can be displaced from saturated clay soil by movement of an organic fluid into the soil. As the organic fluid moves through a fluid-conducting pore, incompressible water is displaced. By itself, this does not change interlayer spacing, but the new pore fluid may cause movement of water from non-conducting pores and interlayer spaces to satisfy equilibrium water content of the intruding organic fluid. Since water is usually adsorbed to clay surfaces in multiple layers, the most tightly adsorbed surface layers of water need not be replaced for there to be change in interlayer spacing.

Water displacement would first affect interlayer spacing of clay particles immediately adjacent to or lining pores through which organic fluids were moving. With a compacted clay liner, water would be expected to move from other portions of the liner to re-establish equilibrium interlayer spacing that previously existed in the clay soil. However, if interlayer spacing changes in clays coating or adjacent to pores also caused structural rearrangement of clay particles, changes in interlayer spacing might be irreversible.

TABLE 6. INTERLAYER SPACINGS OF CLAY MINERALS WITH WATER AS THE ADSORBED FLUID PHASE*

	Exchangeable Cation[x]			
Clay Mineral	Li	Na	Mg	Ca
Smectite	2.20	1.90	1.90	1.90
Illite[1]		1.43	1.43	
Kaolinite[2]	0.72	0.72	0.72	0.72
Halloysite (Hydrated)[3]	1.01	1.01	1.01	1.01

* Brown (1961)

[x] Monovalent cations may result in extensive interlayer swelling beyond the values given

[1] Normally potassium is non-exchangeably adsorbed yielding an interlayer spacing of 1nm.

[2] Protons are usually the interlayer cations since hydrogen bonding prevents interlayer separation

[3] Metahalloysite (dehydrated) yields interlayer spacings approximating that of kaolinite

A combination of interlayer spacing decrease and particle rearrangement by organic fluids could cause change in effective pore diameter and hence overall permeability of the clay. A factor of 4 increase in a fluid conducting pore diameter is depicted in Fig. 9. Such increase in pore diameter would increase permeability by a factor of 256.

If the intruding organic fluid had an appreciable dipole moment, the amount of water solubilized would be greater than if the fluid were non-polar. However, polarity also gives the organic fluid ability to directly replace water in interlayer spaces. This effect would negate some interlayer spacing decreases expected from removal of interlayer water.

Water can be replaced in capillary pores (micropores), interlayer spaces, and interlayer surfaces by cationic and strongly polar organic fluids. The strength of the water retention by clays is determined by the hydration energy of interlayer cations, adsorption energy of the water on interlayer surfaces, and ability of water to bridge across capillary pores by a network of hydrogen bonds. Water could be replaced in micropores and interlayer spaces by disruption of structuring generated by the network of hydrogen bonds. If this occurred, resulting interlayer spacing of the clay would be a complex function of several interacting fluid properties affecting the balance of attractive and repulsive forces between clay layers.

Forces of attraction, represented by the London-van der Waals forces, are strongest close to the clay surface and diminish rapidly with increasing distance form the surface. Values of these attractive forces at given distances from the surface do not vary significantly with changes in environmental context. An explanation of theory underlying this force has been written by Van Olphen (1963).

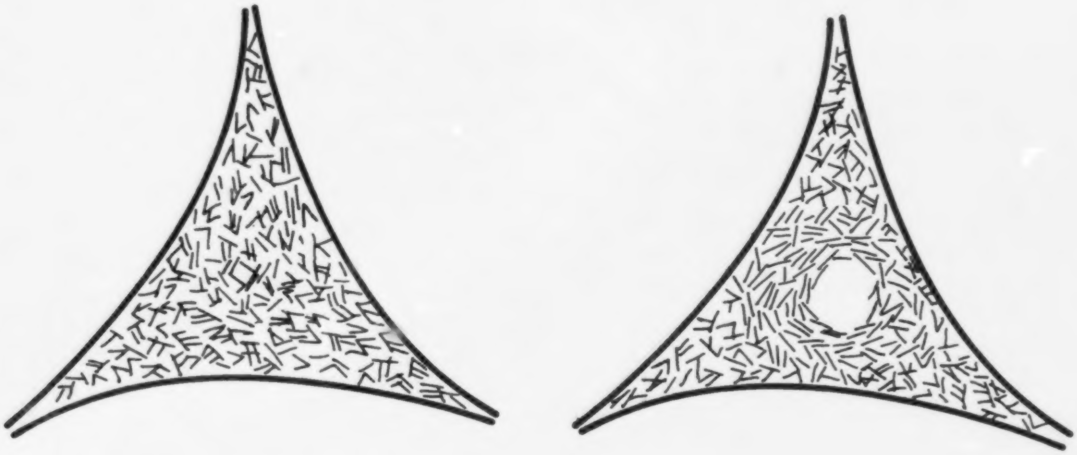


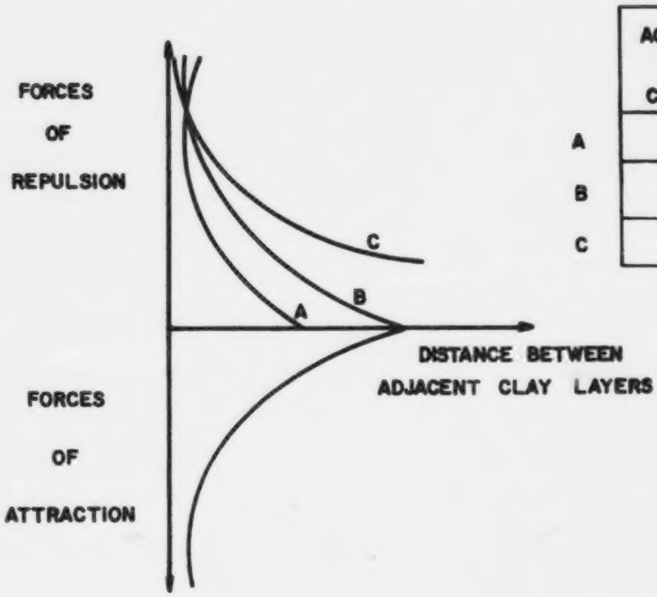
FIG. 9. Change in a Pore Diameter (400%) Corresponding to a Permeability Increase of 25,600%

Forces of repulsion between clay layers are determined by several factors such as salt concentration, dielectric constant, and dipole moment of the fluid in the interlayer. Effects of salt concentration and dielectric constant on repulsive forces are schematically represented in Fig. 10. Weiss (1958) noted the direct relationship between salt concentration and interlayer spacing of smectites in a study utilizing distilled water and several concentrations of sodium chloride in water. Both distilled water and 0.01N NaCl gave infinite interlayer spacing values (the clay was completely dispersed), while 1.0, 3.0 and 5.0N NaCl gave interlayer spacings of 1.92, 1.60, and <1.57 nm respectively. Yong and Warkentin (1975) found that at interlayer spacings less than 1.5 nm, attractive forces between clay particles were greater than the repulsive forces. As the concentration of salt dissolved in the interlayer space increases, the repulsive forces (represented by thickness of the electrical double layer) are diminished. If the salt concentration in an interlayer fluid is high enough to cause the attractive forces to exceed the repulsive forces between clay particles, the clay will tend to flocculate. This could change a dispersed, structureless, and slowly permeable clay soil into an aggregated, structured, and more permeable one.

An analogous situation could occur where interlayer water is displaced by an organic fluid that has a lower dielectric constant than water (Figure 10). Theory of dielectric constant has been thoroughly explained by Bockris and Reddy (1970). Simply stated, the dielectric constant represents the ability of a fluid to transmit charge through itself. As this ability decreases (i.e., decreasing dielectric constant), the fluid film surrounding the clay and containing positive cations must be thinner for the negative surface charge on the clay to be neutralized.

Due to the effects of dielectric constant on the electrical double layer, there is a relationship between the dielectric constant of an adsorbed fluid and interlayer spacing exhibited by clay particles. In general, interlayer spacing decreases with decrease in the dielectric constant (Table 7). This apparent relationship is complicated by a number of other factors such as the dipole moment of a fluid (Barshad, 1952), interlayer cation of the clay (Bissada et al., 1967), degree of methyl substitution on the organic molecule (Olejnik et al., 1970), and ion-dipole interactions (Czarnecka and Gillott, 1980). Most studies of various factors affecting interlayer spacing, however, have been limited to situations dealing with clay surfaces following pretreatments such as dehydration prior to immersion in test fluids (Barshad, 1952).

In one study that has some applicability to hydrated systems, the clays were dehydrated prior to the study but then immersed in a mixture of water and an organic fluid (Barshad, 1952). The dehydrated clays were immersed in 100% water and various mixtures of water and propanol to obtain interlayer spacing for the clay exposed to a fluid series with decreasing dielectric constant (Table 8). As predicted, interlayer spacing exhibited by calcium saturated smectite decreased with decreases in dielectric constant of the fluid mixture. The same author performed a similar study obtaining similar results with water-glycerol mixtures.


FORCES
OF
REPULSION
C
B
A
DISTANCE BETWEEN
ADJACENT CLAY LAYERS
FORCES
OF
ATTRACTION

	AQUEOUS SYSTEM (SALT CONCENTRATION)	ORGANIC FLUIDS (DIELECTRIC CONSTANT)
A	HIGH	LOW
B	MEDIUM	MEDIUM
C	LOW	HIGH

FIG. 10. Forces Between Clay Surfaces as Affected by Salt Concentration and Dielectric Constant

TABLE 7. INTERLAYER SPACING OF CALCIUM SMECTITE AS A FUNCTION OF DIELECTRIC CONSTANT AND DIPOLE MOMENT*

Interlayer Spacing	Sorbed Fluid	Dipole Moment	Dielectric Constant
0.99	Benzene	0	2.3
0.99	Paraffin	0	2.1
1.45	Butanol	1.6	17.7
1.70	Ethanol	1.7	25.0
1.71	Methanol	1.6	32.4
1.73	Methyl Ethyl Ketone	2.7	18.9
1.92	Water	1.8	78.5

From Barshad (1952)

* All samples were dehydrated at 250°C prior to immersion in the test fluid.

TABLE 8. INTERLAYER SPACING OF CALCIUM SMECTITE[+] IMMERSED IN FLUIDS OF VARIOUS DIELECTRIC CONSTANTS*

Immersion Liquid	Dielectric Constant (25°C)	Interlayer Spacing (nm)
100% water	78.5	1.92
70% water-30% propanol	57.7	1.88
40% water-60% propanol	36.4	1.84
30% water-70% propanol	30.7	1.77
20% water-80% propanol	26.1	1.77
10% water-90% propanol	22.7	1.52
100% propanol	20.1	1.44
100% water	78.5	1.92
40% water-60% glycerol	59.4	1.79
100% glycerol	39.2	1.68

* Modified from Barshad (1952)

[+] Dehydrated at 250°C prior to immersion in liquid.

The dipole moment of a fluid also affects interlayer spacing by affecting the number of fluid layers that will form on clay surfaces. MacEwan (1951) found that the number of fluid layers in smectites increased with increasing dipole moment and decreasing molecular size. Strongly polar fluids, such as nitromethane and acetonitrile, were found to form more than two layers (MacEwan, 1948).

While interlayer spacing resulting from intercalation of a given compound increases with increasing molecular size, the number of fluid layers that will adsorb to a clay surface decreases with increases in molecular size. This phenomenum explains the initial increase in interlayer spacing from methanol through ethanol which are small enough to adsorb in two layers (Table 9). However, members of the homologous series larger than ethanol are restricted to adsorbing in one layer. Thus from ethanol to propanol, there is an initial decrease in interlayer spacing corresponding to one adsorbed layer. Following this initial decrease, the interlayer spacing gradually increases with increasing molecular size of the adsorbed alcohol. The decrease from two to one adsorbed fluid layer is due both to the increase in molecular size and the decrease in dipole moments and dielectric constants of the large alcohols.

In comparing the interlayer spacings for an organic fluid adsorbed at different dehydration temperatures (Table 10), several interesting trends can be observed. Dehydration at higher temperatures removes more of the

TABLE 9. CHANGES OF INTERLAYER SPACING IN SMECTITE WITH A HOMOLOGOUS SERIES OF NORMAL MONOHYDRIC ALCOHOLS*

Normal Monohydric Alcohols	Spacing Between Layers (nm)	Thickness of One Layer (nm)	Number of Adsorbed Layers
Methanol[1]	0.74	0.37	2
Ethanol[1]	0.79	0.39	2
1-Propanol[2]	0.45	0.45	1
1-Butanol[2]	0.46	0.46	1
1-Pentanol[2]	0.46	0.46	1
2-Methyl-2-Butanol[2]	0.54	0.54	1
Cyclohexanol[2]	0.54	0.54	1

* From MacEwan (1948)

[1] Treated with large excess of cold liquid

[2] Boiled down to half volume with excess of liquid

TABLE 10. INTERLAYER SPACINGS FOR ORGANIC FLUIDS AT DIFFERENT (PRETREATMENT) DEHYDRATION TEMPERATURES*

Interlayer Spacing (nm)	Adsorbed Fluid	Dipole Moment (debyes)	Dielectric Constant	Dehydration Temperature (°C)
0.99	Paraffin	0	2.1	250
1.45	n-Butanol	1.66	17.7	250
1.45	Paraffin	0	2.1	20
1.52	n-Butanol	1.66	17.7	20
1.92	Water	1.84	78.5	250

* From: Barshad (1952)

strongly adsorbed interlayer water. Subsequent treatment with organic fluids yields lower interlayer spacings for clays dehydrated at the highest temperature. This is also true, but to a lesser degree, when sodium rather than calcium is the interlayer cation. When clay is dehydrated at room temperature (20°C) there is still water coating its surfaces. However, both a neutral polar compound, n-butanol, and a neutral nonpolar mixture, paraffin, reduce interlayer spacing of clay dehydrated at 20°C as compared to clay treated with water after dehydration. This indicates that even compounds less attracted to clay surfaces than water can displace some interlayer water and thus decrease interlayer spacing. Such common neutral nonpolar organic solvents such as xylene, benzene, heptane, or paraffin oil have potential for decreasing interlayer spacings in clay liners.

Concentration of organic compounds in interlayer spaces of clay has been found to affect preferred compound orientation and hence resultant interlayer spacing. In a study conducted with fully hydrated smectite, Greene-Kelly (1955) found that the slightly basic aromatic compound aniline adsorbed with aromatic rings parallel to the clay surface at low concentrations (0.62 meq/gm clay) resulting in low interlayer spacing (1.42 nm). Orientation of the aromatic compound became perpendicular at higher concentrations (0.91 meq/gm clay) and resulted in higher interlayer spacings (1.78 nm).

Assessment of effects of organic fluids on initially "water-wet" clay in clay liners is complicated by the complexity of interactions between clay surfaces and resulting interlayer spacing changes. An increase in energy is required to dehydrate the clay surface (Gh), repel water from the interlayer space (Gp), and dissociate an organic fluid molecule from other organic molecules in the flowing phase (Gd) in order to penetrate to the clay surface. However, energy is decreased when the organic fluid is adsorbed by the London-van der Waals forces (Gs) or associated with the oxygen on the clay surface (Ga). Such energy decreases would increase the likelihood of an organic molecule penetrating the inner Helmholtz layer (V), which is the layer immediately adjacent to the surface of a clay.

Penetration of the inner Helmholtz layer by an organic cation is promoted by an increase in molecular charge (Z) or an increase in inner Helmholtz electrical potential (Y). Regardless of type of organic fluid, its ability to penetrate to the surface of a clay is greatly enhanced by increasing its concentration (X). An equation relating the above variables, temperature (T), and the Boltzmann constant (k) has been given by Yariv and Cross (1979) as follows:

$$V = X\exp-(YZ + \Delta G_a + \Delta G_s - \Delta G_d - \Delta G_h - \Delta Gp)/kT$$

It is next to impossible to quantitate several of the above variables even in carefully controlled laboratory experiments. Obviously, the task would be even harder in the actual environment of an in-place clay liner exposed to a complex mixture of organic compounds. One important factor that can be gleaned from the equation, however, is that potential for inner Helmholtz layer penetration by organic molecules normally excluded from clay surfaces is greatly enhanced if the molecule is in high concentration.

The reason for concern about changes in interlayer spacing of clay is the impact the changes may have on permeability of a clay liner. No studies have been found that examine the relationship between interlayer spacing and permeability. However, by combining information found in several studies, a relationship can be deduced. Decreasing dielectric constant or dipole moment of an adsorbed fluid has been found to decrease interlayer spacing of clays (Barshad, 1952) and yield a clay with increased permeability (Michaels and Lin, 1954).

PERMEABILITY MEASUREMENTS OF CLAY SOILS

Permeability (K) describes the rate at which a fluid can move through a porous matrix (Fetter, 1980). Darcy (1856) was first to systematically study the relationships between flux of a liquid through a porous matrix (J in $cm^3\ cm^{-2}\ sec^{-1}$), volumetric liquid flow (Q in $cm^3\ sec^{-1}$), the hydraulic gradient (H), cross sectional area of liquid flow (A in cm^2), and the permeability constant for a given porous matrix (K in $cm\ sec^{-1}$). These parameters are related through Darcy's Law:

$$J = \frac{Q}{A} = KH$$

Hydraulic gradient (H) is defined as the ratio of the difference in hydraulic head between the top and bottom of the porous matrix (Δh in cm of H_2O), and the length of the porous matrix over which the liquid flows (l in cm). This infers that volumetric liquid flow (Q) is proportional to the difference in fluid head (Δh) and inversely proportional to flow length (l) where flow is laminar. Hydraulic gradient (H) can be expressed as follows:

$$H = \frac{h\ (top) - h(bottom)}{l} = \frac{\Delta h}{l}$$

Volumetric liquid flow (Q) is simply volume of liquid (v in cm^3) which moves through the porous matrix in a given time (t in seconds), and expressed as follows:

$$Q = \frac{v}{t}$$

Combining the above variables, the permeability constant of a porous matrix can be expressed as follows:

$$K = \frac{v\ l}{A\ t\ \Delta h}$$

To normalize the permeability constant (K) for flow of fluids with various viscosities (μ expressed as $gm\ cm^{-1} sec^{-1}$) and densities (ρ in $gm\ cm^{-3}$), the intrinsic permeability constant (k in cm^2) can be calculated from the permeability constant (K) of a porous matrix as follows:

$$k = \frac{K\mu}{\rho g}$$

where g is the gravitational constant of 983 cm sec^{-2}. The viscosity parameter normalizes resistence to flow of a fluid due to cohesiveness, while the density parameter normalizes the effect of gravity. As the above equation indicates, permeability of a porous matrix is directly proportional to density and inversely proportional to viscosity of the permeant fluid (Fetter, 1980).

One assumption of Darcy's Law is that fluid flow is laminar rather than turbulent (Bear, 1972). Bowles (1979) stated that turbulent flow would occur in pipes above a hydraulic gradient of 2,100, and in presumably sandy soils at hydraulic gradients as low as 300-600. Hubbert (1956) studied flow in a bed of cylinders and found that Darcy's Law broke down at hydraulic gradients greater than 600. He found the "cause of the failure of Darcy's Law is the distortion that results in the flowlines when the velocity is great enough that the inertial force becomes significant." Rumer (1964) concluded that "the limit of validity of Darcy's Law is not because of the inception of turbulence but is due to the increasing influence of the inertia forces." These inertial forces become significant before flow is turbulent in the nonlinear laminar flow regime.

The use of large hydraulic gradients has shortcomings. The thickness of immobilized fluid films on soil particles would be substantially decreased at large pressures (Yong and Warkentin, 1975). This would increase effective pore diameter available for fluid flow and thus permeability. On the other hand, large hydraulic gradients can increase soil particle migration causing soil clogging and a resulting decrease in permeability (Olson and Daniel, 1979).

Criteria for selecting an appropriate hydraulic gradient greatly depends on proposed use of the permeability study. Where the objective is to estimate field permeability values, it has been suggested "to use gradients as close to those encountered in the field as is economically feasible" (Olson and Daniel, 1979). Zimmie et al. (1981) suggested use of hydraulic gradients between 6 and 20 for laboratory studies attempting to duplicate field conditions.

In comparative permeability studies, larger hydraulic gradients may be used. Care should be taken, however, to maintain linear laminar flow and monitor for particle migration. Comparative studies often use permeant fluids that may change permeability of a soil (Michaels and Lin, 1954). Hydraulic gradients used should be far enough below the turbulent flow threshold to maintain linear laminar flow after permeability increases. If permeability of a clay soil increases enough for flow to become turbulent at the hydraulic gradient utilized, subsequently obtained permeability values may be invalid even for comparative purposes.

Laboratory permeability studies can be used to estimate permeability in the field or to evaluate relative effects of different factors on permeability of a clay liner. The former is by far more difficult to perform due to difficulty in exactly duplicating field conditions. Comparative permeability studies can be performed more easily since rigorous duplication of field conditions are not essential so long as flow is laminar and particle migration is minimal.

Several authorities on permeability studies have expressed doubts that laboratory permeability tests are capable of reproducing field conditions. Olson and Daniel (1979) noted that the volume of soil samples used in laboratory tests are almost always too small to contain statistically significant distributions of macrofeatures encountered in the field (i.e., sand lenses, fissures, joints, channels, root holes, etc.). They further noted that samples taken in the field may be affected either by collection method or selection of the most uniform or intact sample. Bowles (1978) stated that "The soil in the permeability device is never in the same state as in the field—it is always disturbed to some extent." Zimmie et al. (1981) stated that "It is virtually impossible to duplicate field hydraulic gradients in the laboratory. Test times become excessive and it becomes difficult to obtain accurate measurements of flows and heads at very low hydraulic gradients."

Several factors not incorporated into laboratory tests affect overall permeability of clay. Sherard and Decker (1977) listed primary factors determining "effective overall permeability" of a soil layer as being continuity, regularity, thickness, and characteristics of interbeded layers or lenses. Laboratory permeability determinations on clay liners cannot account for this type of variability and can only attempt to characterize a homogeneous sample of clay soil. Other factors that may lead to discrepancies between field and laboratory permeability values are discussed in detail by Olson and Daniel (1979).

Comparative permeability studies utilize multiple permeameters to isolate effects of one or more variables. This testing approach has been widely used in agricultural irrigation studies evaluating the influence of various salt types and concentrations on soils of low permeability (McIntyre et al., 1979; McNeal, 1974). Comparative methods have also been used to evaluate the influence of organic fluids on soils (Michaels and Lin, 1954; Van Schaik, 1970).

Permeability tests conducted for this study are strictly comparative in nature and do not attempt to reproduce typical field conditions. The aim of this study is to investigate the potential influence of various organic fluids on permeability of compacted clay soils. Except where noted in the discussion of test results, effects of factors other than soil-fluid interactions are considered to be eliminated through establishment of baseline permeabilities for each sample using 0.01N $CaSO_4$ as initial permeant fluid.

Testing procedures used in this study are not suitable for exact determinations of field permeability values. They are, however, considered suitable for performing rapid comparative studies to evaluate the potential influence of waste fluids on permeability of compacted clay soil liners. As there is a large variety of waste fluids placed in hazardous waste landfills and surface impoundments (Table 2), there is a great need for a qualitative permeability test which can rapidly determine potential effects these fluids may exert on permeability of clay liners. As waste fluids listed in Table 2 are but a fraction of fluid-bearing waste types disposed in industrial landfills, rapid qualitative permeability tests that can be performed easily by laboratory technicians may be the only feasible method for evaluating the impact of hazardous wastes on clay liner integrity.

To simplify laboratory personnel training and allow intercalibration by independent laboratories, a qualitiative permeability test method should use standardized procedures and readily available apparatii. The test method developed for this study was designed with these objectives in mind.

In comparative permeability studies, flow should be laminar, and all but the variable being tested should be constant. Under these conditions, any change in permeability is the result of changes in the porous matrix. Yong and Warkentin (1975) noted that aside from independent fluid and soil properties, permeability of a soil is affected by forces holding a fluid to soil particles and soil-fluid interactions. They further noted that relative influence of any one factor on permeability was difficult to assess since many are interdependent.

SECTION 4

MATERIALS AND METHODS

To understand factors influencing permeability of clay liners to organic fluids, it was necessary to construct a functional perspective. This perspective includes the following components:

1. Delineation of physical classes of organic liquid-bearing hazardous wastes.

2. Description of leachates generated by various waste classes.

3. Interpretation of fluid types contained by various waste leachates.

4. Evaluation of characteristics of clay soils used to line disposal facilities.

5. State-of-the-art review of mechanisms involved in interaction between organic fluids and clay soils that may alter permeability of clay liners.

With this perspective as a guide, representative organic fluids and clay soils were selected, and methodology was developed appropriate for evaluating the influence of organic fluids on permeability of compacted soils.

FLUIDS STUDIED

Seven organic fluids representing four classes of organic fluids and water (Figure 5) were selected for use in comparative permeability studies. The four classes of organic fluids studied were acidic, basic, neutral polar, and neutral nonpolar. Table 11 lists the seven organic fluids and water along with their relevant physical and chemical properties.

Organic fluids used in this study were reagent grade (pure). Actual waste leachates are normally a mixture of fluids combined with various organic and inorganic solutes. In addition, waste leachates often contain particles in suspension that could clog or coat soil pores. While pure organic fluids would not usually be discarded, pure fluids were used in

TABLE 11. ORGANIC FLUIDS AND WATER: RELEVANT PHYSICAL AND CHEMICAL PROPERTIES

FLUIDS		Temp. Range of Fluid State (°C)		Density at 20°C (gm/cm^3)	Viscosity at 20°C (Centipose)	Dielectric Constant at 20°C	Water Solubility at 20°C (gm/1)	Dipole Moment (debyes)	Molecular Weight
Organic Fluid	Name	Melting Point	Boiling Point						
Acid, Carboxylic	Acetic Acid (Glacial)	17	118	1.05	1.28	6.2	miscible	1.04	60.1
Base, Aromatic Amine	Aniline	-6	184	1.02	4.40	6.9	34.0	1.55	93.1
Neutral Polar, Alcohol	Methanol	-98	65	0.79	0.54	31.2	miscible	1.66	32.0
Neutral Polar, Ketone	Acetone	-95	56	0.79	0.33	21.4	miscible	2.74	58.1
Neutral Polar, Glycol	Ethylene Glycol	-13	198	1.11	21.0	38.7	miscible	2.28	62.1
Neutral Nonpolar, Alkane	Heptane	-91	98	0.68	0.41	2.0	0.003	0.0	100.2
Neutral Nonpolar, Alkyl-Benzene	Xylene	-47	139	0.87	0.81	2.4	0.20	0.40	106.2
Water		0	100	0.98	1.0	80.4		1.83	18.0

this study to eliminate variables other than fluid properties that could affect the resulting permeability values.

Glacial acetic acid was selected to represent the acidic organic fluid class. Organic acids are byproducts of several industrial processes and of anaerobic decomposition processes that occur in landfills. Acetic acid is fluid at room temperature with a density and viscosity somewhat greater than that of water. The dielectric constant is significantly lower, and dipole moment is only slightly lower than values exhibited by water. Acetic acid is infinitely soluble in water.

Aniline is a slightly basic organic fluid at room temperature and substantially soluble in water. It is considerably more viscous and only slightly more dense than water. As with acetic acid, aniline has a dielectric constant much lower and dipole moment slightly lower than values exhibited by water.

Three neutral polar organic fluids studied are fluid at room temperature and infinitely soluble in water. Values for other properties decrease in the following orders:

Density: Ethylene Glycol >Water >Acetone=Methanol
Viscosity: Ethylene Glycol >>Water >Acetone >Methanol
Dielectric Constant: Water >>Ethylene Glycol >Methanol >Acetone
Dipole Moment: Acetone >Ethylene Glycol >Water >Methanol

Two neutral nonpolar organic fluids studied are fluid at room temperature and very sparingly soluble in water. Values for other properties of these fluids decrease in the following orders:

Density: Water >Xylene >Heptane
Viscosity: Water >Xylene >Heptane
Dielectric Constant: Water >>Xylene >Heptane
Dipole Moment: Water >>Xylene>Heptane

Water (0.01N $CaSO_4$) was used as control fluid to establish baseline permeability of each soil core. The calcium salt was selected due to its stabilizing effect on permeability. Concentration of 0.01N was selected because it approximates salt concentrations typically found in soils.

CLAY SOILS STUDIED

Four native clay soils with diverse mineralogical or chemical properties were selected for this study. Two of the soils had predominantly smectitic clay minerals but different chemical properties. Two other soils contained predominantly kaolinitic and illitic clay minerals, respectively. Additionally, each soil was characterized by the following:

1. Exhibited permeability less than 1×10^{-7} cm sec^{-1} when compacted at optimum water content.

2. Had a geographic extent of at least one million hectares.

3. Existed in deposits thick enough to permit economic excavation for use as clay liners.

4. Contained a minimum of 35% (by weight) clay minerals.

Following collection, the clay soils were broken into golf ball size clods and air dried. The soils were then ground sufficiently to pass through an ASTM Number 4 sieve (4.75 mm) and stored at room temperature in large drums prior to testing. Methods for determining soil propeties used by Soil Physics Laboratories at Texas A&M University are described by Black (1965) except for moisture-density relations where ASTM methods were used.

General information on the four soils is given in Table 12. This includes soil series and order, its location geographically and within the solum, and the parent material from which each soil was derived.

Table 13 gives grain size distribution of the soils and the mineralogy of the clay sized fraction. Native clay deposits seldom contain only one type of clay mineral, and these four clay soils are no exception. The mixed cation kaolinitic soil contains two predominant clay mineral species (kaolinite and halloysite). Clay sized quartz is present in all soils to varying extents.

Physical properties of the four clay soils are given in Table 14. Properties determined for the soils in undisturbed states included shrink-swell potential, permeability, color, corrosivity, and structure. Other properties determined on remolded soil samples included liquid limit plasticity index, water retention, optimum moisture content, and maximum dry density. Other values for physical properties of the remolded soils can be found in Appendix B.

Chemical properties of the four soils are given in Table 15. The distinction between noncalcareous and calcareous smectites arises from values for total alkalinities of 3.3 and 129.2 meq/100g respectively. The calcareous nature of the latter is further illustrated by its content of 33% by weight calcium carbonate.

Other chemical properties of especially high potential for influencing permeability include the 3% organic matter content of the calcareous smectite and the 13.2% Fe_2O_3 content of the mixed cation illite. (The kaolinitic and illitic clay soils were given the prefix "mixed cation" because no specific cation predominates on their exchange sites).

Optimum water content for obtaining maximum dry density of a soil subjected to a given compactive effort was determined for the four soils using ASTM 698-70. Several compacted soil cores prepared for optimum water content determinations were also utilized to determine the influence of compaction water content on permeability of the soils to water (0.01N $CaSO_4$). Figs. 11-18 show the resulting moisture-density-permeability

TABLE 12. GENERAL PROPERTIES OF THE FOUR CLAY SOILS

Clay Soil Description	Noncalcareous(1) Smectite	Calcareous(1) Smectite	Mixed Cation(1) Kaolinite	Mixed Cation(2) Illite
Soil Series	Lufkin	Houston Black	Nacogdoches	Hoytville
Soil Order	Alfisol	Vertisol	Alfisol	Alfisol
Horizon	B_{21tg}	A_{11}-A_{12}	B_{21t}-B_{22t}	B_{21g}-B_{22g}
Location in Solum (cm)	18-51	0-61	15-178	20-67
Parent Material	Slightly acid to alkaline clayey sediments.	Calcareous clays and marls.	Old Marine sediments high in glauconite.	Calcareous silty clay, glacial till.
Geographic Setting	Upland with 0-3% sope.	Upland with 0-8% slope.	Upland with 0-15% slope.	Lake plain with 0-2% slope.
Extens (Ha)	>2.2 million	5.5 million	>1.1 million	>2.3 million
General Location	East Central Texas	Blackland Praries of Texas	Coastal Plains of Texas	Northwestern Ohio
Type Location	Brazos County, Texas, 500 m south of FM 60, 1 km west of College Station.	Bell County, Texas, from intersection of US 190 and Texas 36, go 1000 m southeast on Texas 95, and go 800 m west northwest.	Nacogdoches County, Texas, from a road cut on the right hand side of Hwy 105 going west, 20 km west of Nacogdoches.	Wood County, Ohio, on the grounds of the Northwestern Branch of Ohio Agricultural Res. and Dev. Center near Hoytville.

(1) Soil Conservation Service (1976)
(2) Blevins and Wilding (1968).

TABLE 13. GRAIN SIZE DISTRIBUTION OF THE FOUR CLAY SOILS AND MINERALOGY OF THE CLAY SIZED FRACTIONS*

Clay Soil Description	Noncalcareous Smectite	Calcareous Smectite	Mixed Cation Kaolinite	Mixed Cation Illite
% Sand (>50 nm)	35-37	7-8	39-41	14-15
% Silt (50-2.0 nm)	26-28	42-44	17-18	38-39
% Clay (<2.0 nm)	36-38	48-50	42	47
Coarse Clay (2.0-0.2 nm)				
% of Total	16 (1)	25 (1)	33 (1)	61 (2)
Mineralogy (3)	QZ-1 KK-2 MI-2	MT-1 KK-2 QZ-3	KK-1 QZ-2	I-1 QZ-2
Fine Clay (<0.2 nm)				
% of Total	84 (1)	75 (1)	67 (1)	39 (2)
Mineralogy (3)	MT-1	MT-1 KK-3	KH-1 MI-3	I-1 MT-2

* All data from Soil Physics Laboratories, Texas A&M University unless otherwise noted.

(1) Soil Conservation Service (1976).
(2) Blevins and Wilding (1968).
(3) Key to Mineralogy Data:

MT = Smectite
KK = Kaolinite
I = Illite
QZ = Quartz
MI = Mica or Illite
KH = Halloysite

1 = >40%
2 = 10-40%
3 = <10%

TABLE 14. PHYSICAL PROPERTIES OF THE FOUR CLAY SOILS*

Clay Soil Description	Noncalcareous Smectite	Calcareous Smectite	Mixed Cation Kaolinite	Mixed Cation Illite
Shrink-Swell Potential	very high	very high	moderate	moderate
Permeability ($cmsec^{-1}$)**	$<4.5 \times 10^{-5}$	$<4.5 \times 10^{-5}$	4.5×10^{-4}	4.5×10^{-4}
Liquid Limit	51-67	58-98	41-60	$\sim$46 (1)
Plasticity Index	30-45	34-72	18-30	$\sim$27 (1)
Color (dry)	grayish brown	very dark gray	dark red	gray (1)
Corrosivity (steel)	high	high	high	N.D.
Water Retention at 1/3 bar^{+}	31.0 (2)	48.0 (2)	21.0 (2)	30.0 (2)
Optimum Water Content^{++}	20.0 (2)	21.5 (2)	20.0 (2)	19.0 (2)
Maximum Density ($kN\ m^{-3}$)	15.0 (2)	14.4 (2)	16.3 (2)	16.6 (2)
Structural Description	Prismatic to blocky, vertical cracks 2 cm wide.	Blocky, cracks 1-10 cm wide when dry.	Blocky, friable when moist, hard when dry.	Moderate to strong, fine to medium angular blocky.

* All data from Soil Conservation Service (1976) unless otherwise noted.

(1) Blevins and Wilding (1968)

(2) Soil Physics Laboratories, Texas A&M University

N.D. Not Determined.

** Undisturbed State.

+ % by Weight.

++ % by Dry Weight.

TABLE 15. CHEMICAL PROPERTIES OF THE FOUR CLAY SOILS*

Clay Soil Description	Noncalcareous Smectite	Calcareous Smectite	Mixed Cation Kaolinite	Mixed Cation Illite
Cation Exchange Capacity (meq/100 gm)	24.2	36.8	8.6	18.3
Exchangeable Cations (meq/100 gm)				
Na	1.4	1.4	0.1	0.1
K	0.3	1.0	0.2	0.4
Ca	18.5	51.8 (3)	1.3	17.3
Mg	6.3	1.8	1.4	3.0
Water Soluble Cations (meq/100gm)				
Na	0.49	0.84	0.33	0.62
K	0.22	0.27	0.12	1.86
Ca	<0.01	0.25	0.02	0.03
Mg	0.04	0.06	<0.01	0.09
Total Alkalinity (meq/100 gm)	3.3	129.2	0.8	4.2
pH (saturated paste)	6.1	7.9	5.1	7.5
Ec (mmhos/cm)	0.2	0.4	<0.1	0.2
Fe_2O_3 (%)	0.42 (1)	0.2 (1)	13.2 (2)	-
Organic Matter (%)	0.9 (1)	3.0 (1)	0.6 (2)	-
$CaCO_3$ Equiv. (%)	-	33 (2)	Trace (2)	-

* All data from Soil Physics Laboratories, Texas A&M University unless otherwise noted.

(1) Davidson and Page (1956).

(2) Derendinger (1968).

(3) Calcium value is high due to dissolution of $CaCO_3$ by the extracting solution used (1.0N Ammonium Acetate at a pH of 7).

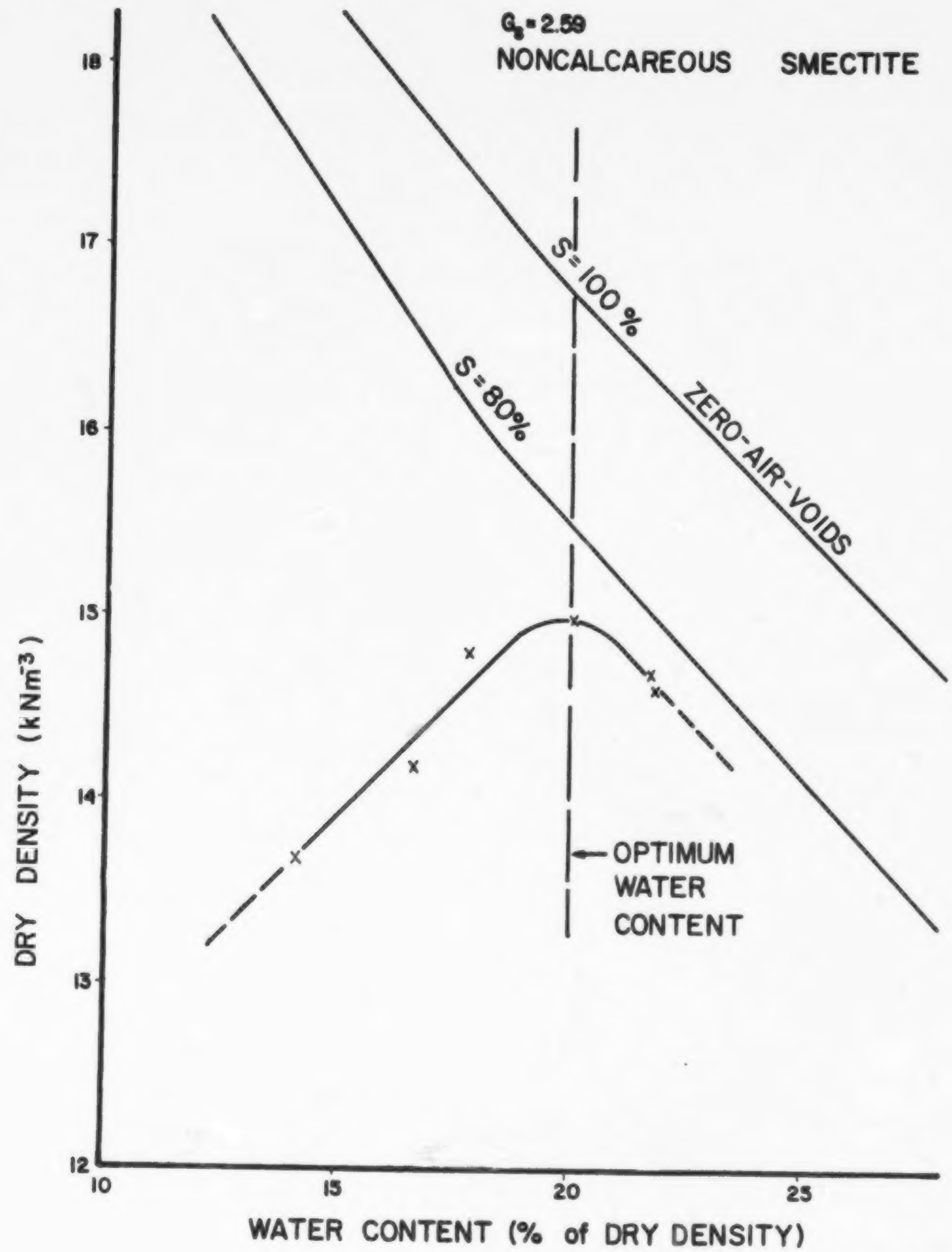


FIG. 11. Compaction Moisture Content-Density Relationship for the Noncalcareious Smectitic Clay Soil

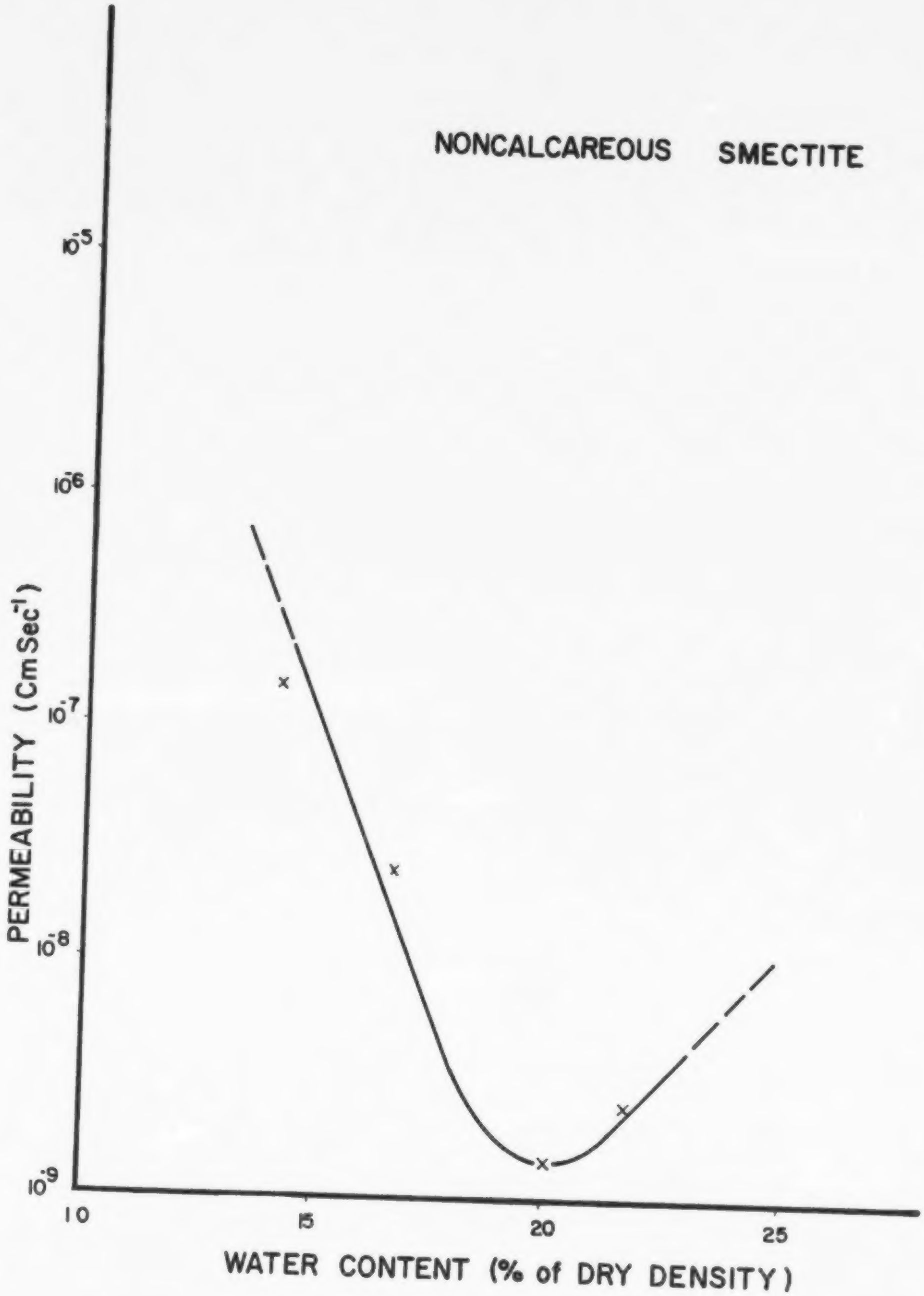


FIG.12. Compaction Moisture Content-Permeability Relationship for the Noncalcareous Smectitic Clay Soil

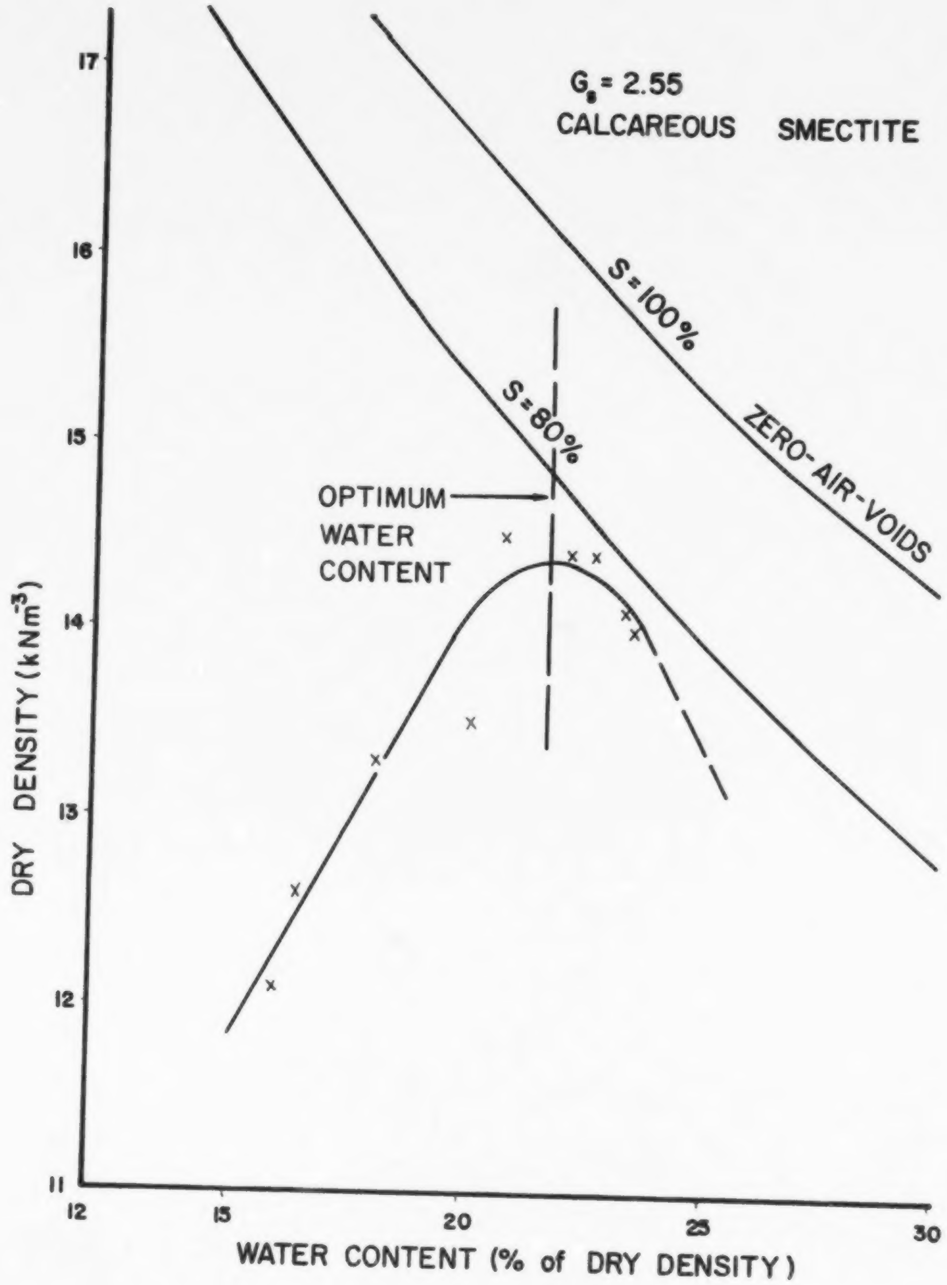


FIG. 13. Compaction Moisture Content-Density Relationship for the Calcareous Smectitic Clay Soil

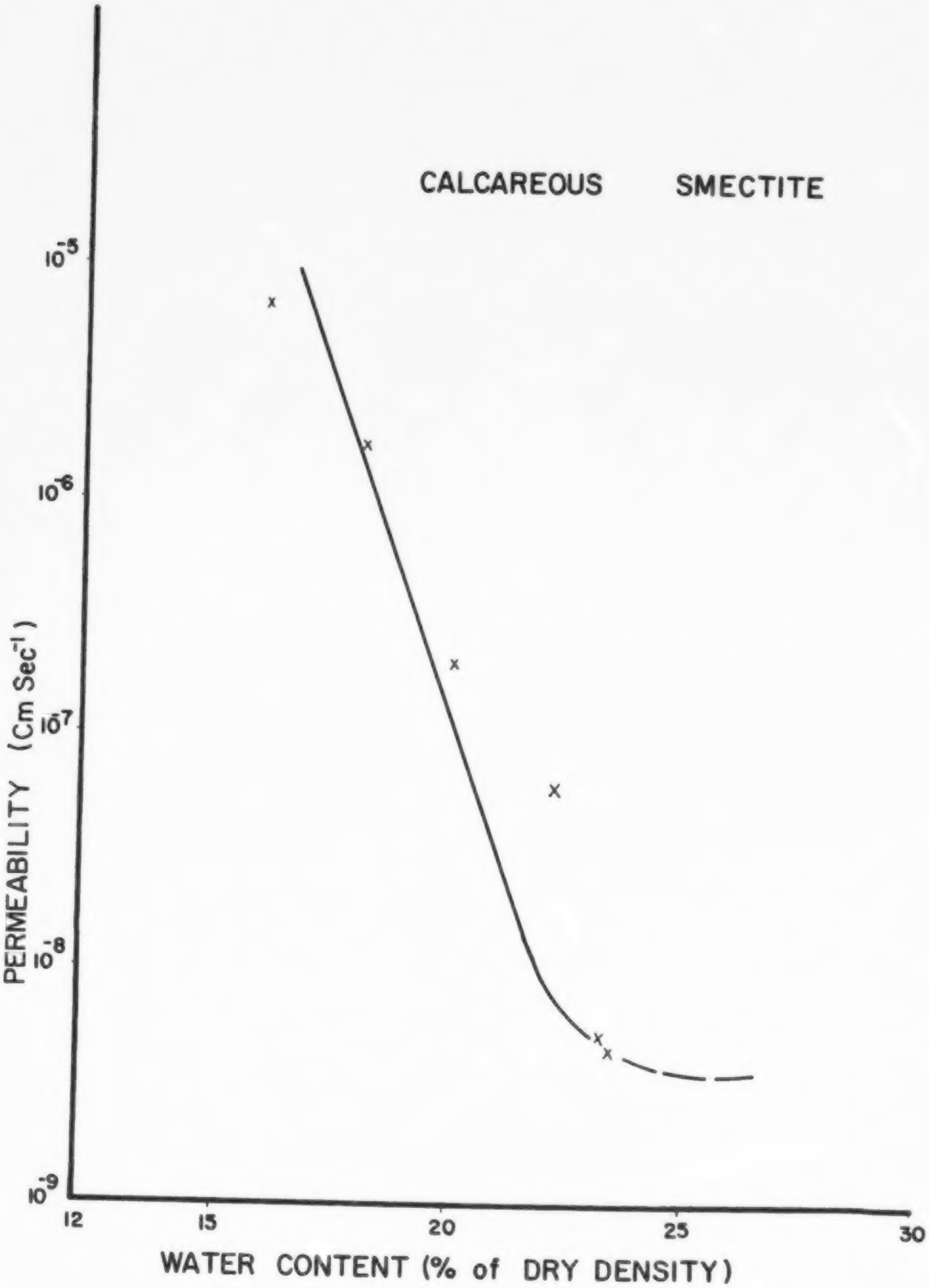


FIG. 14. Compaction Moisture Content-Permeability Relationship for the Calcareous Smectitic Clay Soil

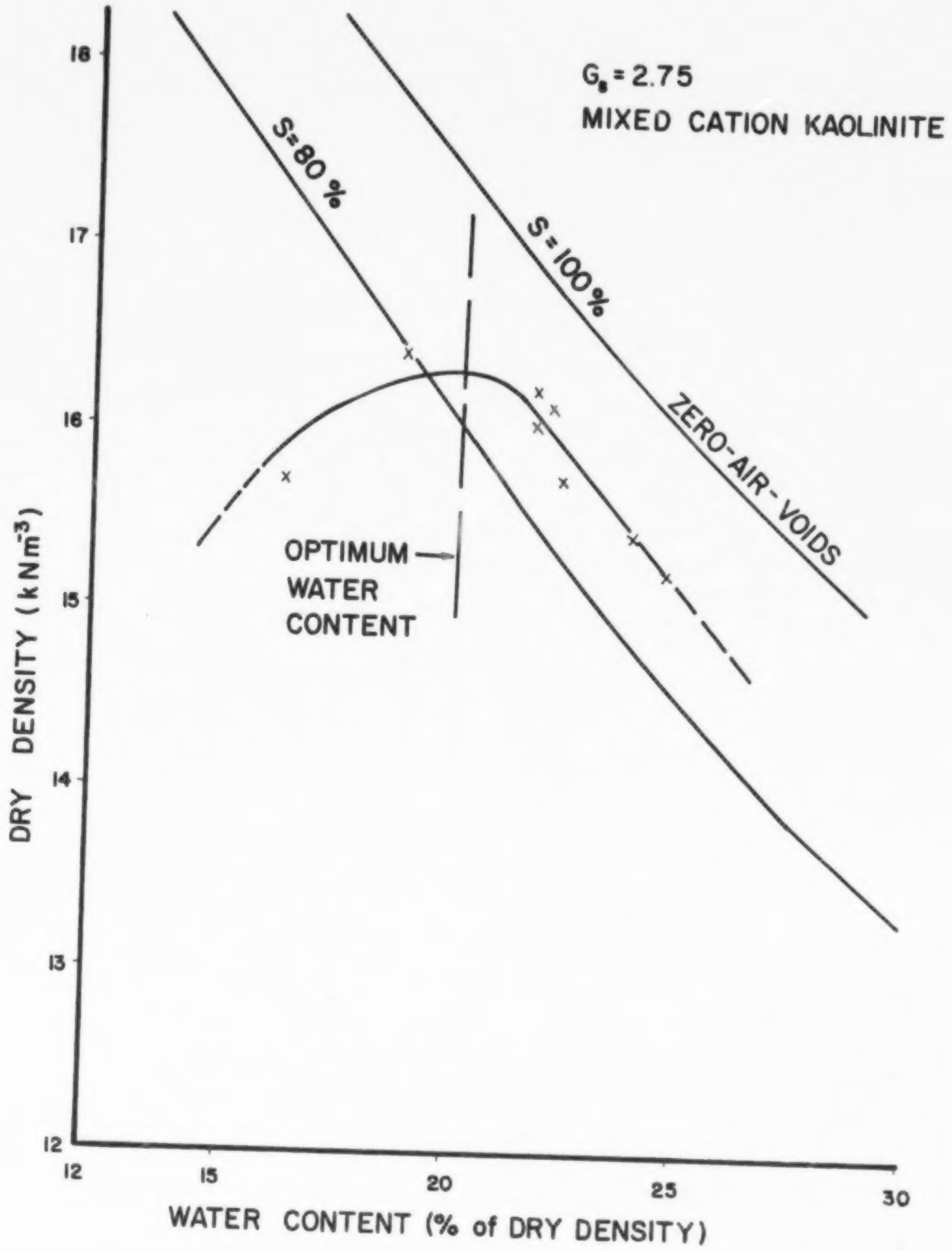


FIG. 15. Compaction Moisture Content-Density Relationship for the Mixed Cation Kaolinitic Clay Soil

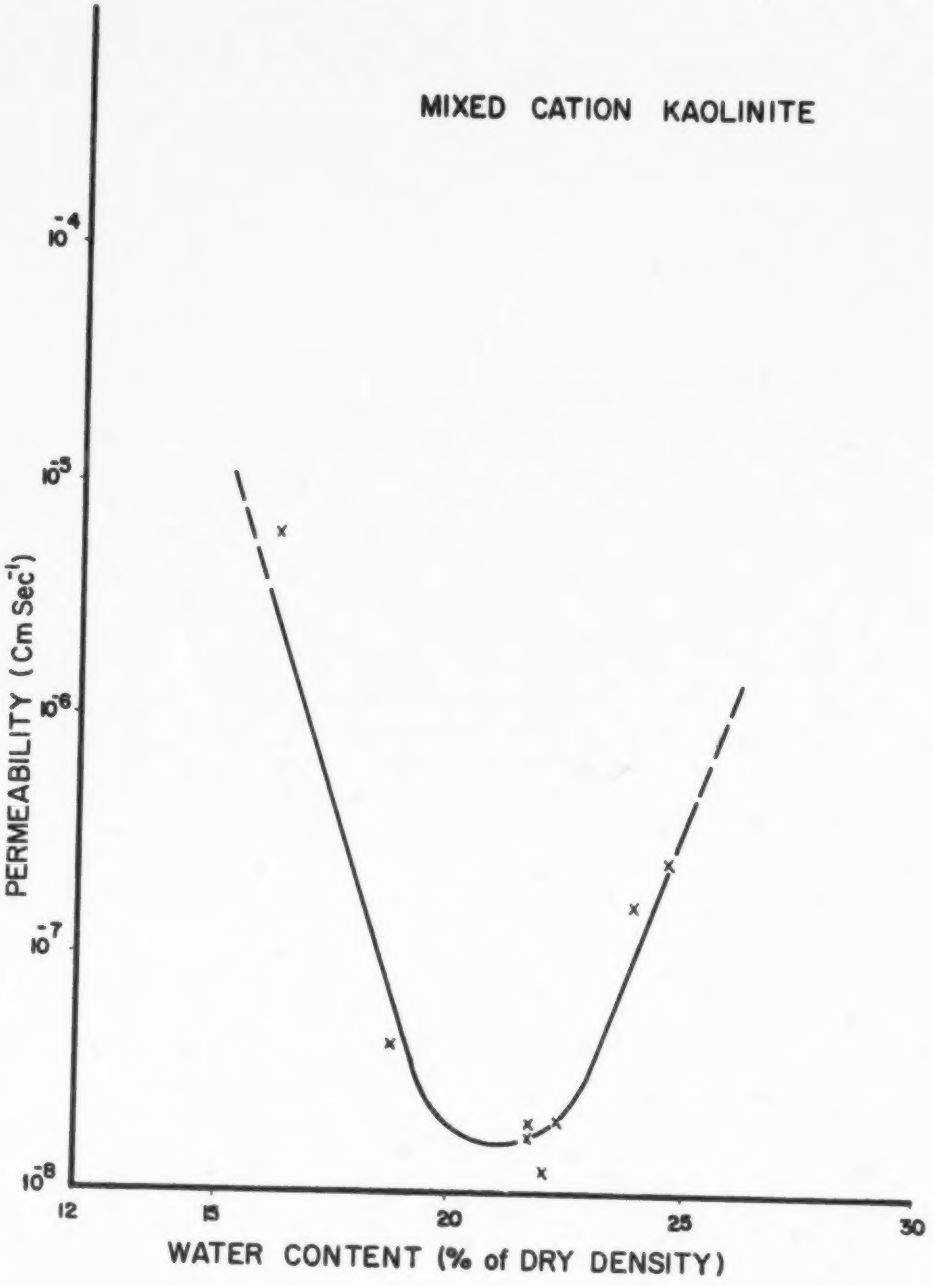


FIG. 16. Compaction Moisture Content-Permeability Relationship for the Mixed Cation Kaolinitic Clay Soil

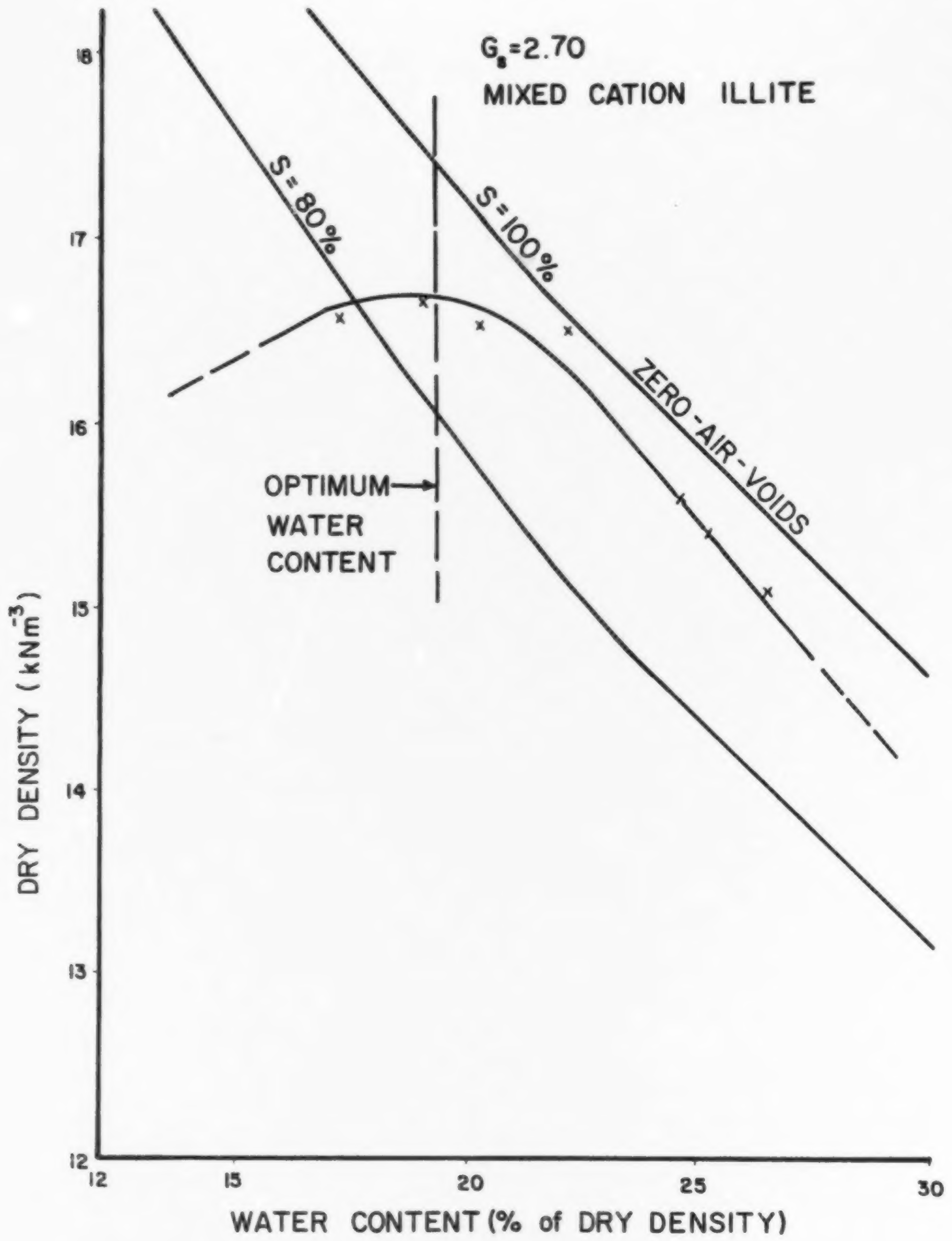


FIG. 17. Compaction Moisture Content-Density Relationship for the Mixed Cation Illitic Clay Soil

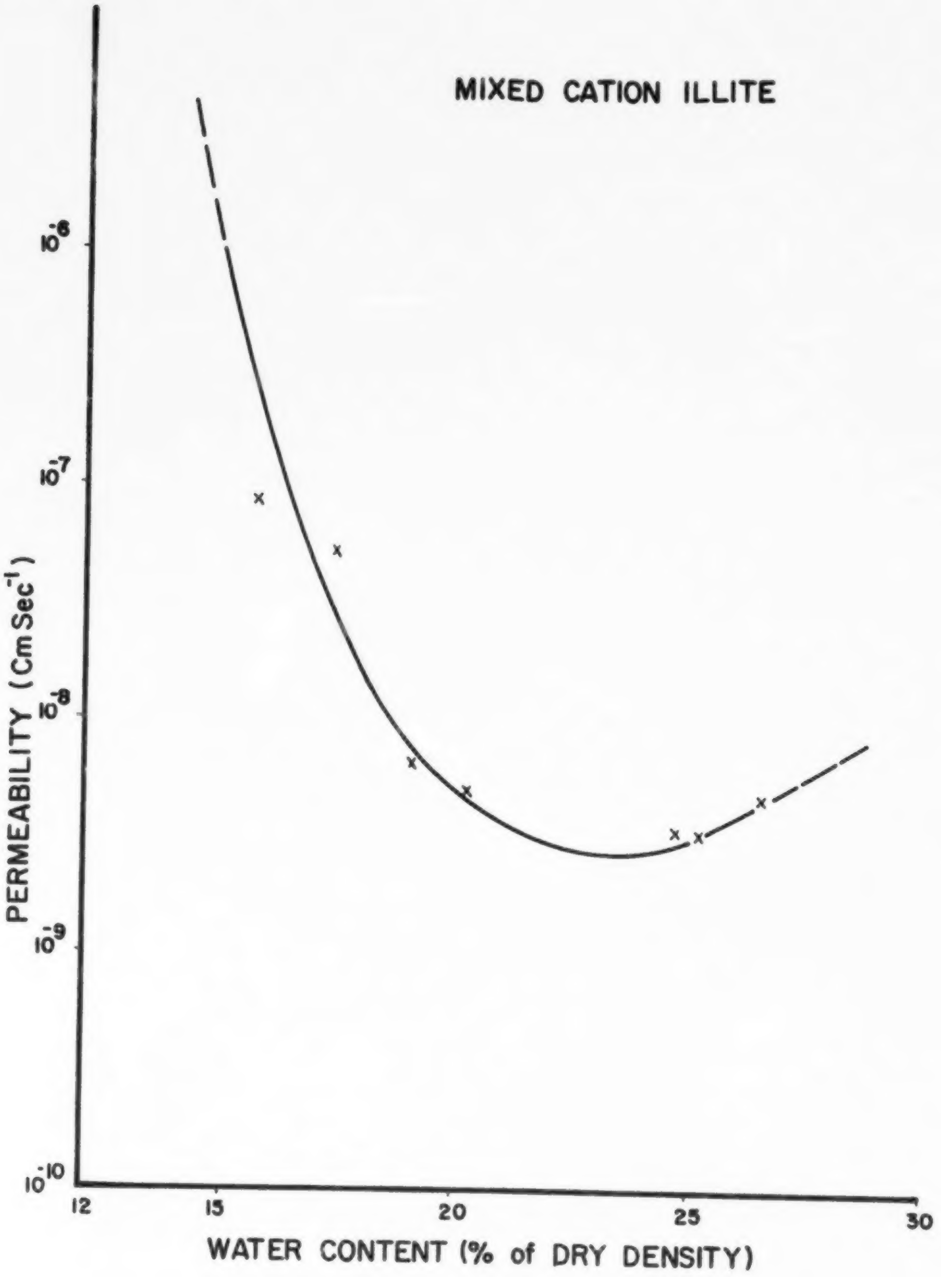


FIG. 18. Compaction Moisture Content-Permeability Relationship for the Mixed Cation Illitic Clay Soil

relationships of the four clay soils. Data used in these figures is given in Appendix A.

Percentage of soil voids filled with water after compaction at optimum moisture content was approximately 75% and 90% for the two smectitic and the other two clay soils respectively. The minimum permeability value for each clay was found to occur at or just above the optimum moisture content. Particle densities (Gs) of the four clay soils are given on the moisture-density graphs.

PERMEABILITY TEST CONSIDERATIONS, CALCULATIONS AND PROCEDURES

Tests on soils of low permeability must be carefully performed to be accurate. Leaks, trapped air, volatile losses, and turbulent flow or channeling along the soil chamber wall can greatly affect permeability values (Bowles, 1978). Each of these sources of error was considered in the development of permeability test procedures. In addition, steps were taken to minimize inherent dangers associated with organic fluids under pressure.

Compacted clay soils often have permeability values lower than 10^{-8} cm sec^{-1}, and it may be necessary to pass a pore volume of water through a soil before a stable baseline permeability value is obtained. After establishing the permeability baseline, the passage of at least a pore volume of organic test fluid may be necessary to fully determine effects the fluid may have on permeability of the compacted clay soil. Consequently, a pressurized air source has been used to increase the hydraulic gradient and reduce time needed for testing (Bennett, 1966; Jones, 1960).

Additionally, trapped air has been a common cause for artificially low permeability values (Christiansen et al., 1946). Increasing the pressure head exerted on a soil core reduces trapped air by increasing the weight of gas that will dissolve in water flowing through the core (Jones, 1960). Elevated pressure also reduces volume of remaining air pockets.

A pressurized air-induced, elevated hydraulic gradient was used in the comparative permeability tests of the compacted clay soils. A hydraulic gradient of 361.6 (equivalent to a hydraulic head of 42.2 m of H_2O) was used for the two smectitic clay soils. A hydraulic gradient of 61.1 (equivalent to a hydraulic head of 7 m of H_2O) was used for the illitic and kaolinitic clay soils.

To avoid channel formation, the compacted clay soils were seated at a hydraulic gradient of 1.85 (10 cm H_2O). By letting 10 cm of standard leachate stand on the soils for 48 hours, an effective seat was obtained for the top few millimeters of soil. This thin layer prevented bulk flow, thereby permitting the rest of the soil to adequately seal the permeameter sidewalls at elevated pressures.

The form of Darcy's Law used to calculate permeability is as follows:

$$K = \frac{V}{AtH}$$

where:

K = permeability constant (cm sec^{-1})

V = volume of liquid passed through the soil (cm^3)

A = cross-sectional area of liquid flow (80.1 cm^2)

H = hydraulic gradient = $\frac{h+1}{1}$

h = hydraulic head (cm of H_2O)

1 = length of soil (11.7 cm)

Permeability constants obtained with the above equation can be normalized for liquids with various viscosities and densities by multiplying by the density and dividing by the viscosity of the test fluid. By normalizing the impact of viscosity and density on permeability, the influence of other factors on permeability changes can be observed.

Compacted soil cores used to evaluate permeability to organic fluids were prepared at or above optimum water content. Data on these cores are presented in Appendix B. After compaction, the soil cores were mounted on permeameter base plates and fitted with fluid chambers and permeameter top plates (Fig. 19). Each top plate was fitted with a pressure inlet connecting it to a pressurized air source via the pressure distribution manifold (Fig.20).

A moisture and debris trap, pressure regulator, and pressure gauge were placed between the pressurized air source and manifold. The trap was positioned between the air source and regulator to prevent buildup of debris on the regulator membrane. The pressure gauge was placed between the regulator and manifold so that the hydraulic gradient applied to the permeameters could be monitored.

A pressure cutoff valve for each permeameter was placed between the manifold and permeameter top plate. These valves allowed placement or removal of individual permeameters without depressurizing other permeameters.

All gaskets used in the permeameters were teflon to prevent deterioration and possible blowout from contact with various organic fluids. To avoid leakage around the hard teflon gaskets, all metal surfaces against which the gaskets seated were wiped clean of grit. Permeameter components were found to withstand continuous operational use at pressures up to 60 psi (42.2m H_2O).

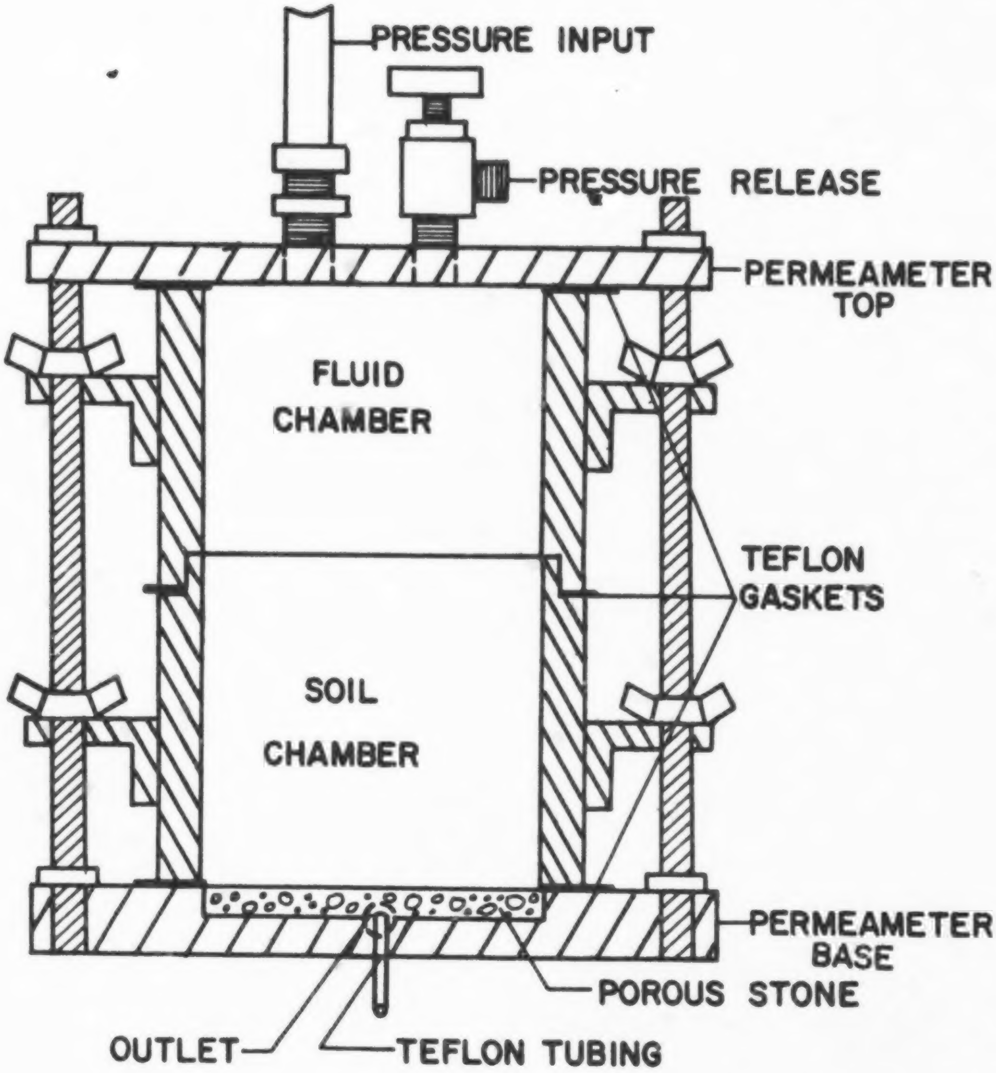

PRESSURE INPUT
PRESSURE RELEASE
PERMEAMETER TOP
FLUID CHAMBER
TEFLON GASKETS
SOIL CHAMBER
PERMEAMETER BASE
POROUS STONE
OUTLET
TEFLON TUBING

FIG. 19. Schematic of the Compaction Permeameter.

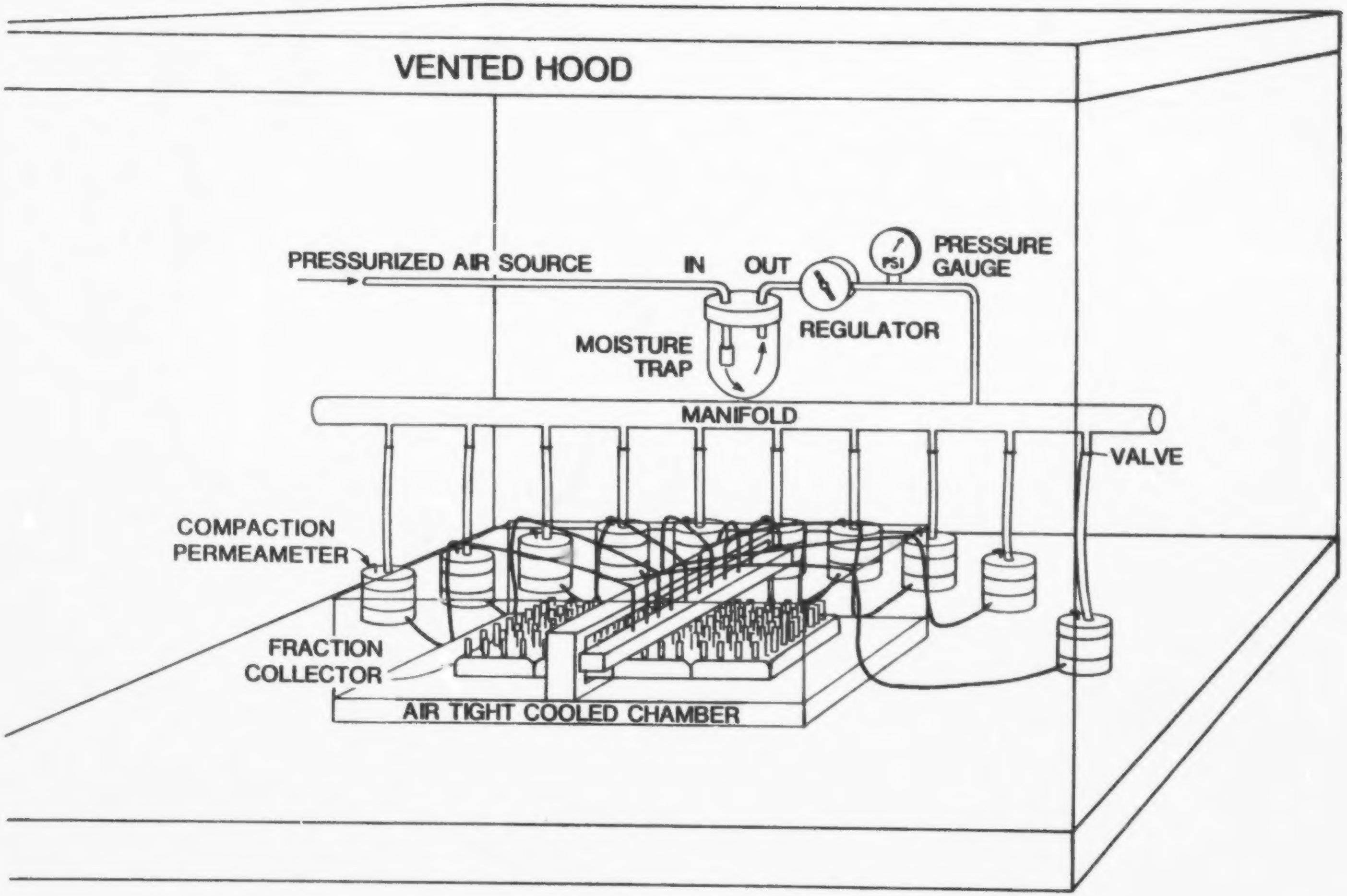

VENTED HOOD
PRESSURIZED AIR SOURCE
IN
OUT
PSI
PRESSURE GAUGE
REGULATOR
MOISTURE TRAP
MANIFOLD
VALVE
COMPACTION PERMEAMETER
FRACTION COLLECTOR
AIR TIGHT COOLED CHAMBER

FIG. 20. Schematic of the Compaction Permeameter Test Apparatus

Directly under the soil chambers and in the permeameter base plates were porous stones to permit seepage of effluent to the base plate outlet. To limit extent of effluent mixing after passage through the compacted soils, the outlet was fitted with an adapter connected to 3 mm inside diameter teflon tubing. The use of translucent teflon at the base plate outlet provided a convenient window with which to monitor expulsion of trapped air. Usually, at least one pore volume of standard leachate (0.01N $CaSO_4$) had to be passed through soil cores before there were no air bubbles visible in the outlet tubing. Where piping occurred in soil cores, eluded soil particles were visible both clinging to the inside walls of the outlet tubing and as a suspension or precipitate in the effluent.

Teflon tubing carried the effluent to an automatic fraction collector which collected effluent samples simultaneously from ten permeameters at specific time increments. Since there was potential for volatile losses during effluent delivery from the tubing to the collection bottles, the top of each bottle was fitted with a long stem funnel, and the fraction collector was placed in a refrigerated, air-tight chamber. Additionally, the entire test apparatus was fitted into a vented hood (Fig. 20). This extra precaution was taken as insurance against worker injury in the event of accidental spills or system leaks.

After seating the soils at low pressure, the selected air pressure was applied to the permeameter fluid chamber until stable permeability values were obtained with the standard leachate. At this point, pressure was released and permeameters disassembled to permit examination of the core for signs of swelling or deterioration. If the soil had expanded out of its mold, the excess was removed with a straight edge while trying not to smear the surface of the soil. The material that had expanded out of the core was oven dried and weighed to estimate percent swelling that had taken place.

With the three soil types that had swollen, additional standard leachate was passed to ensure that permeability was not affected by the excess soil removal. This extra procedural step was not necessary with the kaolinitic soil since it underwent no swelling after passage of standard leachate.

Next, the remaining standard leachate was removed and replaced with the organic fluids for all but the control permeameter. After passage of between 0.5 and 2.0 pore volumes of simulated primary leachates (organic fluids), the permeameters were depressurized, disassembled, and the cores dissected to determine if structural changes had occurred in the compacted clay soils.

For determining breakthrough curves, the percentage of organic fluid in the effluent was determined by one of two methods depending on the fluid analyzed. Immiscible fluids were determined simply by recording the volume of each fluid layer in the sample collection bottles. The only miscible fluid for which determinations were made was methanol. Percent methanol in water was determined using thermoconductivity gas chromatography.

SECTION 5

RESULTS AND DISCUSSION

Permeability values for the clay soils were plotted against cumulative pore volume of test fluid that passed through the compacted core. Volume of effluent was divided by volume of pore space in a given core to obtain the fraction of a pore volume passed at each permeability value. The vertical dashed line on each graph indicates the point at which standard leachate (0.01N $CaSO_4$) was replaced by organic fluids. For several soil cores, breakthrough of organic fluids was plotted across the top of the permeability graphs. All permeability data is given in Appendix C. Following are discussions of effects seven organic fluids and water had on permeability of four clay soils.

WATER (0.01N $CaSO_4$)

Permeability of four compacted clay soils to standard leachate (0.01N $CaSO_4$) are depicted in Fig. 21. Depressurization which occurred at the dashed line appears to have had little effect on permeability. Noncalcareous smectite and mixed cation kaolinite soil permeability values were essentially constant during passage of approximately two pore volumes of standard leachate. In contrast, permeability of calcareous smectite decreased slowly while that of the mixed cation illite increased slowly. Both permeability changes were, however, relatively small.

Relative permeability values for the four clay soils to water are consistent with values typical for those clay types (Fig. 7). Kaolinite exhibited the highest, noncalcareous (partially sodium saturated) smectite showed the lowest, and calcareous (calcium saturated) smectite and mixed cation illite had intermediate permeability.

After passage of two pore volumes of standard leachate, the four clay soils exhibited no visible aggregations and appeared to have retained their initially massive structure. In addition, the surface of the soils showed no signs of large pore development (Fig. 22).

Mean and standard deviation of permeability to water (0.01N $CaSO_4$) for each soil type and individual soil column used in the study are listed in Table 16. Variability in the permeability values was small in all cases. Permeability values of the mixed cation illitic soil exhibited the highest degree of variability of the four clay soil types tested.

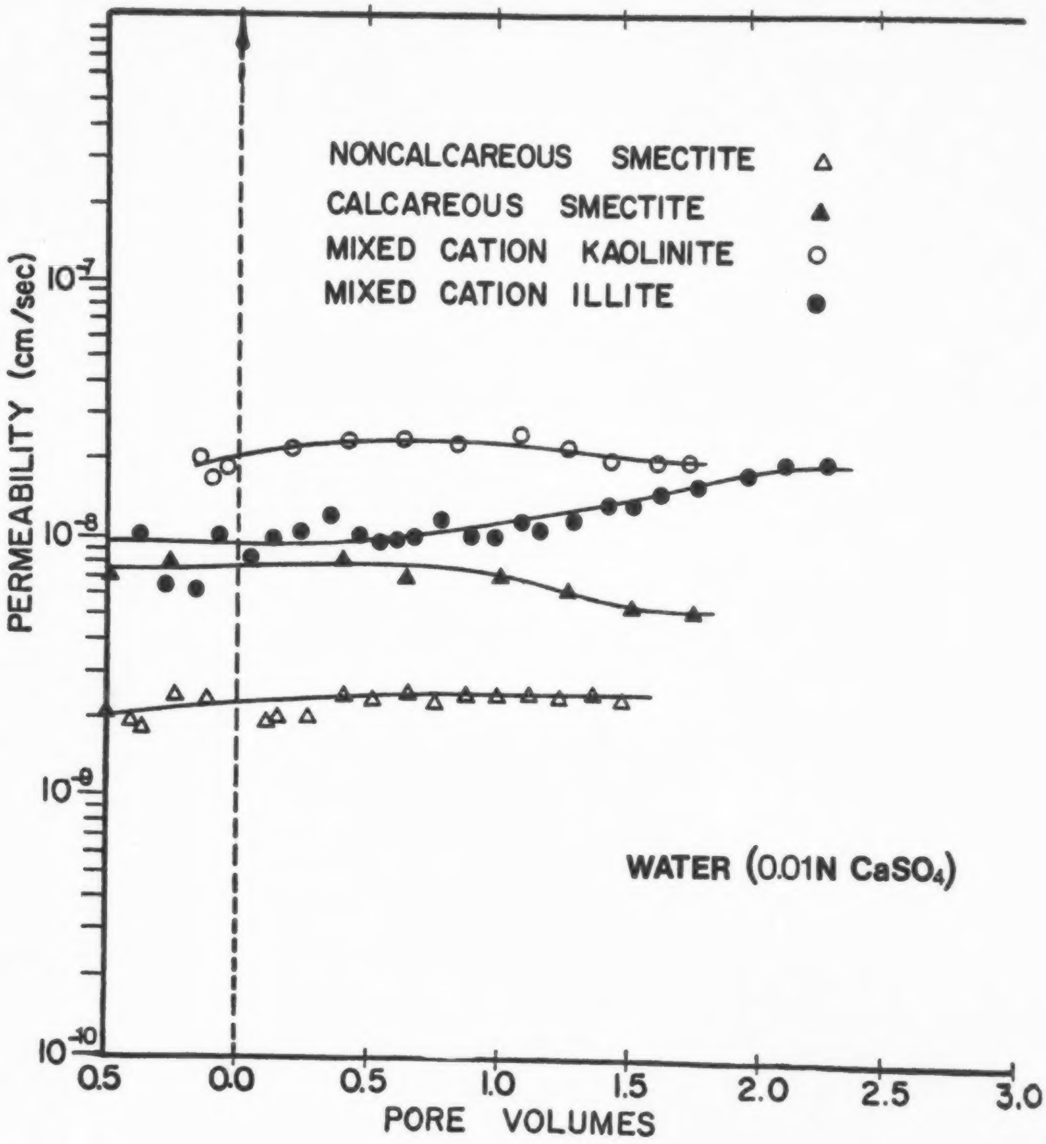


FIG. 21. Permeability of the Four Clay Soils to Water (0.01N $CaSO_4$)

Since permeability of all soil columns were initially determined with water (0.01N $CaSO_4$), the columns were fully saturated prior to exposure to the organic fluids. There are industrial landfills with conditions that may maintain clay liners in an unsaturated state, such as landfills that are in the drier climates prevalent in parts of the western and central U.S. or that have an effective leachate removal system. However, most

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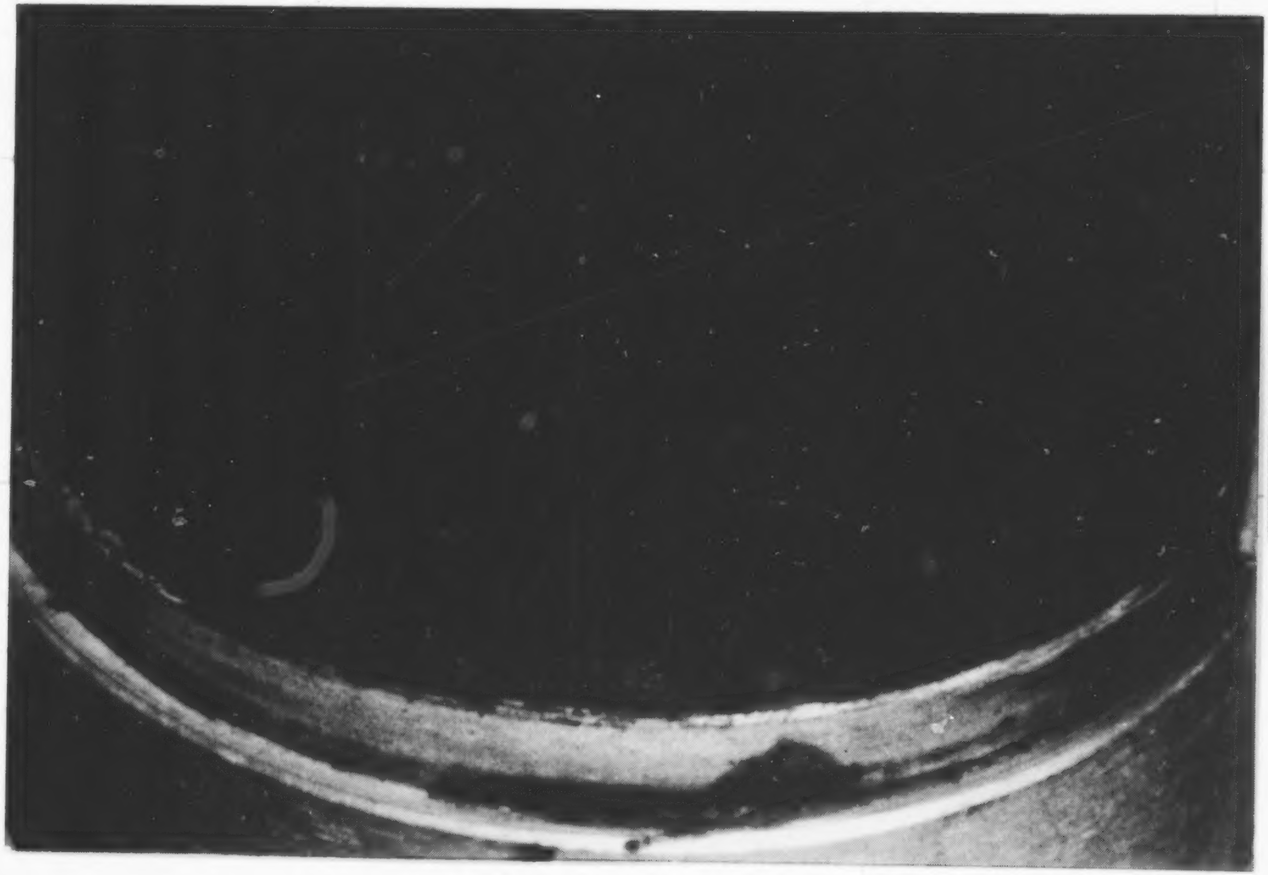

FIG. 22. Surface of the Noncalcareous Smectitic Clay Soil after Passage of Two Pore Volumes of Water (0.01N $CaSO_4$)

TYPING GUIDE SHEET

TABLE 16: PERMEABILITY OF FOUR CLAY SOILS TO WATER ($0.01N CaSO_4$)*

Fluids to Which the Soil Column Would be Exposed	PERMEABILITY (cm sec^{-1})			
	Noncalcareous Smectite	Calcareous Smectite	Mixed Cation Kaolinite	Mixed Cation Illite
Water (0.01N $CaSO_4$)	2.14(±0.26) x 10^{-9}	7.77(±0.64) x 10^{-9}	1.92(±0.18) x 10^{-8}	6.07(±3.88) x 10^{-9}
Acetic Acid	1.59(±0.19) x 10^{-9}	6.48(±0.11) x 10^{-9}	1.30(±0.35) x 10^{-8}	7.31(±0.93) x 10^{-9}
Aniline	2.91(±0.23) x 10^{-9}	3.86(±0.19) x 10^{-9}	1.51(±0.12) x 10^{-8}	3.87(±1.62) x 10^{-9}
Ethylene Glycol	1.39(±0.14) x 10^{-9}	4.67(±0.64) x 10^{-9}	1.55(±0.35) x 10^{-8}	6.75(±1.52) x 10^{-9}
Acetone	1.14(±0.10) x 10^{-9}	3.47(±0.66) x 10^{-9}	2.01(±0.12) x 10^{-8}	3.06(±0.69) x 10^{-9}
Methanol	1.55(±0.17) x 10^{-9}	5.07(±0.52) x 10^{-9}	1.46(±0.42) x 10^{-8}	5.54(±1.52) x 10^{-9}
Xylene	1.44(±0.21) x 10^{-9}	5.62(±0.11) x 10^{-9}	1.77(±0.15) x 10^{-8}	3.51(±1.13) x 10^{-9}
Heptane	1.51(±0.13) x 10^{-9}	3.62(±0.37) x 10^{-9}	1.87(±0.10) x 10^{-8}	4.26(±0.99) x 10^{-9}
All Permeameters	1.63(±0.50) x 10^{-9}	4.98(±1.60) x 10^{-9}	1.71(±0.25) x 10^{-8}	5.14(±2.20) x 10^{-9}

* Values for individual columns represent mean ± one std. dev. of 2-7 permeability measurements. Values given under the designation "All Permeameters" represent mean ± one std. dev. for all soil columns of a given soil type.

industrial landfills are located in relatively wet climates such as the Gulf Coast, Great Lakes, northeast and southeast regions of the U.S. (EPA 1980d, EPA 1980e). These wetter climates would most probably maintain any buried clay soil near saturation.

Traditionally, permeability tests on prospective clay liners for hazardous waste landfills and surface impoundments have used only standard aqueous leachates (such as 0.01N $CaSO_4$ or CaCl) as the permeant fluid. All four of the clay soils used in this study, if only evaluated by this traditional test, would qualify as adequate for lining hazardous waste disposal facilities on the basis of their having permeabilities lower than 1×10^{-7} cm sec^{-1}.

ORGANIC ACID - ACETIC ACID

All four clay soils permeated with acetic acid showed initial decreases in permeability (Fig. 23). However, a significant amount of soil piping occurred in these cores, indicated by soil particles clinging to the inside walls of the outlet tubing and deposited on the bottom of effluent collection bottles. In addition, effluent from these cores was usually tinted (red, creamy, or black) indicating that soil components were dissolved by the acid. Initial decreases in permeability are thought to be due to partial dissolution and subsequent migration of soil particles. These migrating particle fragments could lodge in the fluid conducting pores, thus decreasing crossectional area available for fluid flow.

Two of the soils treated with acetic acid (calcareous smectite and mixed cation kaolinite) showed continuous permeability decreases throughout the test period. After passage of approximately 20% of a pore volume, the acid treated kaolinitic clay generated a dark red colored effluent that smelled of acetic acid. The color was probably due to dissolution of iron oxides which comprise about 13% of the solids in the kaolinitic clay soils. The acid treated calcareous smectite began passing cream colored foamy effluent after passage of about 28% of a pore volume. Since the solid fraction of this clay soil is approximately 33% calcium carbonate, the largest portion of the creamy material was probably dissolved calcium, while the foam was the result of CO_2 liberation from the dissolved carbonates.

Both noncalcareous smectite and the mixed cation illite eventually showed permeability increases after the initial decreases, but the increase did not begin until passage of 39% and 62% of a pore volume respectively. Effluent from the noncalcareous smectitic clay contained soil particles and a black ash-looking material, while effluent from the illitic soil contained red tinted soil particles that became increasingly darker as more effluent was passed. Permeability increases with both of these soils were probably due to progressive soil piping that eventually cleared initially clogged pores.

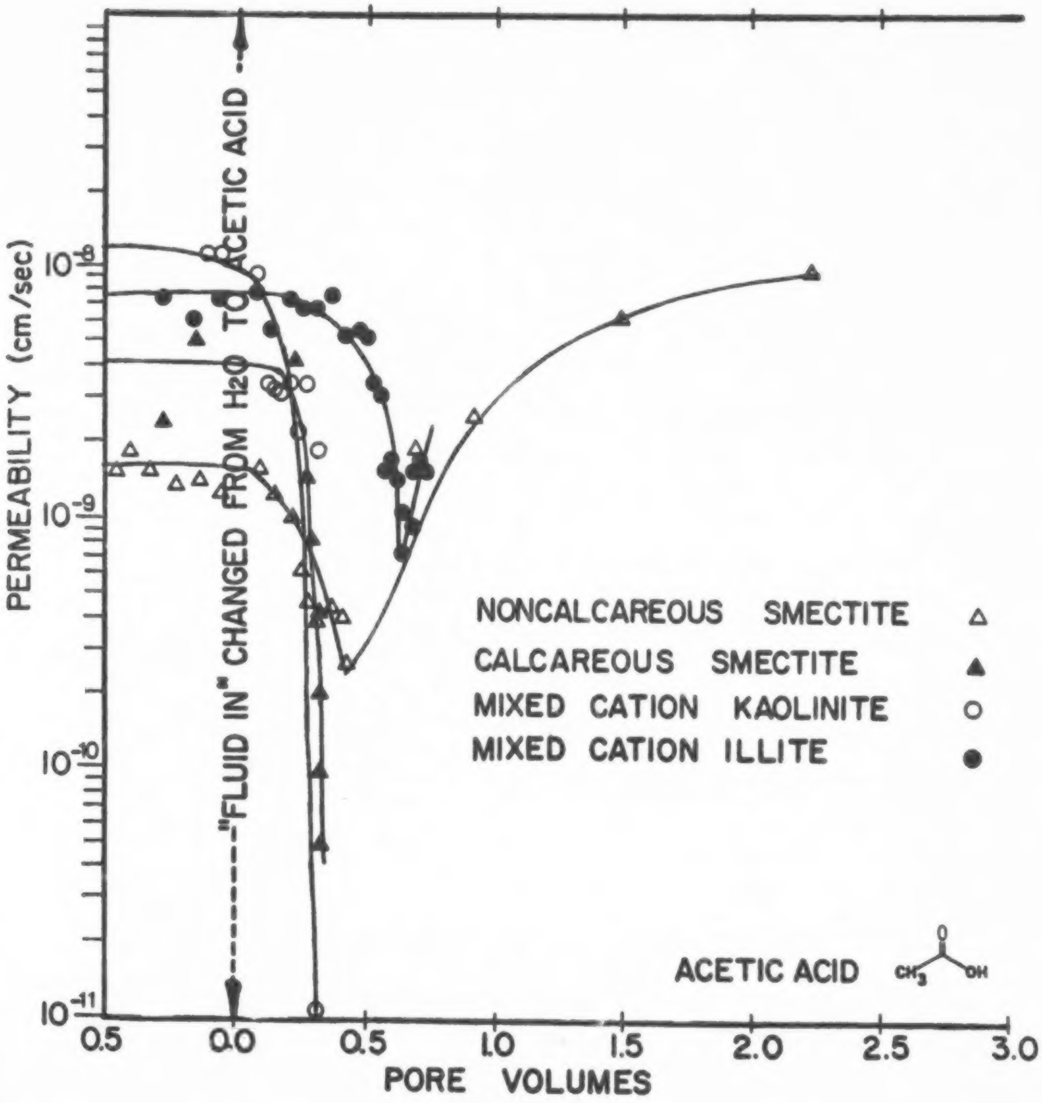

FIG. 23. Permeability of the Four Clay Soils to Acetic Acid

In light of the across-the-board piping that occurred with the acid treated clays, any fluid (such as strong acids and bases) capable of dissolving clay liner components could potentially cause increases in the permeability of the liner. It would seem that neutralization of acids and bases prior to their disposal would be the best safeguard against clay liner failure in these cases.

The density to viscosity ratio of acetic acid (0.82) infers that permeability should decrease approximately 18% from the value obtained with standard leachate. However, the large permeability decreases and subsequent increases (in two of the soils) indicate that soil piping was the predominant influence responsible for permeability changes.

ORGANIC BASE - ANILINE

Permeabilities and breakthrough curves for the four clay soils treated with aniline are given in Fig. 24. While all four clay soils showed significant permeability increases, calcareous smectite showed the least.

Both noncalcareous smectite and mixed cation illite had breakthrough of aniline with concurrent permeability increases at lower pore volume values (<0.5) than the other two clay soils. There was some indication that the permeability of the noncalcareous smectite was reaching a constant value just above 1×10^{-7} cm sec^{-1}.

Permeability climbed above 1×10^{-7} cm sec^{-1} and aniline broke through after passage of one pore volume for the kaolinitic soil. Only the calcareous smectite clay maintained a permeability value below 1×10^{-7} cm sec^{-1}. Its permeability increased rapidly at first, but showed substantial decrease concurrent with aniline breakthrough. After the permeability decrease, this soil exhibited a slow but steady permeability increase.

There were no signs of migrating soil particles in any effluent samples collected from the four aniline treated cores. Apparently, aniline is too weak a base to cause significant dissolution of clay soil components. However, examination of the cores subsequent to the permeability tests indicated that the organic base caused extensive structural changes in the upper half of the soil cores. The massive structure of the four soils after treatment with standard leachate was altered by aniline into an aggregated structure characterized by visible pores and cracks in the surface of the soils [Fig. 25(upper left)]. Fig. 25(upper right) shows aggregated soil removed from the surface of the noncalcareous smectitic clay soil. Fig. 25(lower two) details the platy soil structure exposed by excavation of the soil surface.

According to the equation for intrinsic permeability, a permeant fluid with density and viscosity of aniline should result in soil permeability 77% lower than that obtained with water. However, the four soils tested underwent permeability increases of between 100% and 200% when permeated with aniline. It appears that the predominant factor affecting permeability was the ability of aniline to alter the structural arrangement of particles making up clay soils.

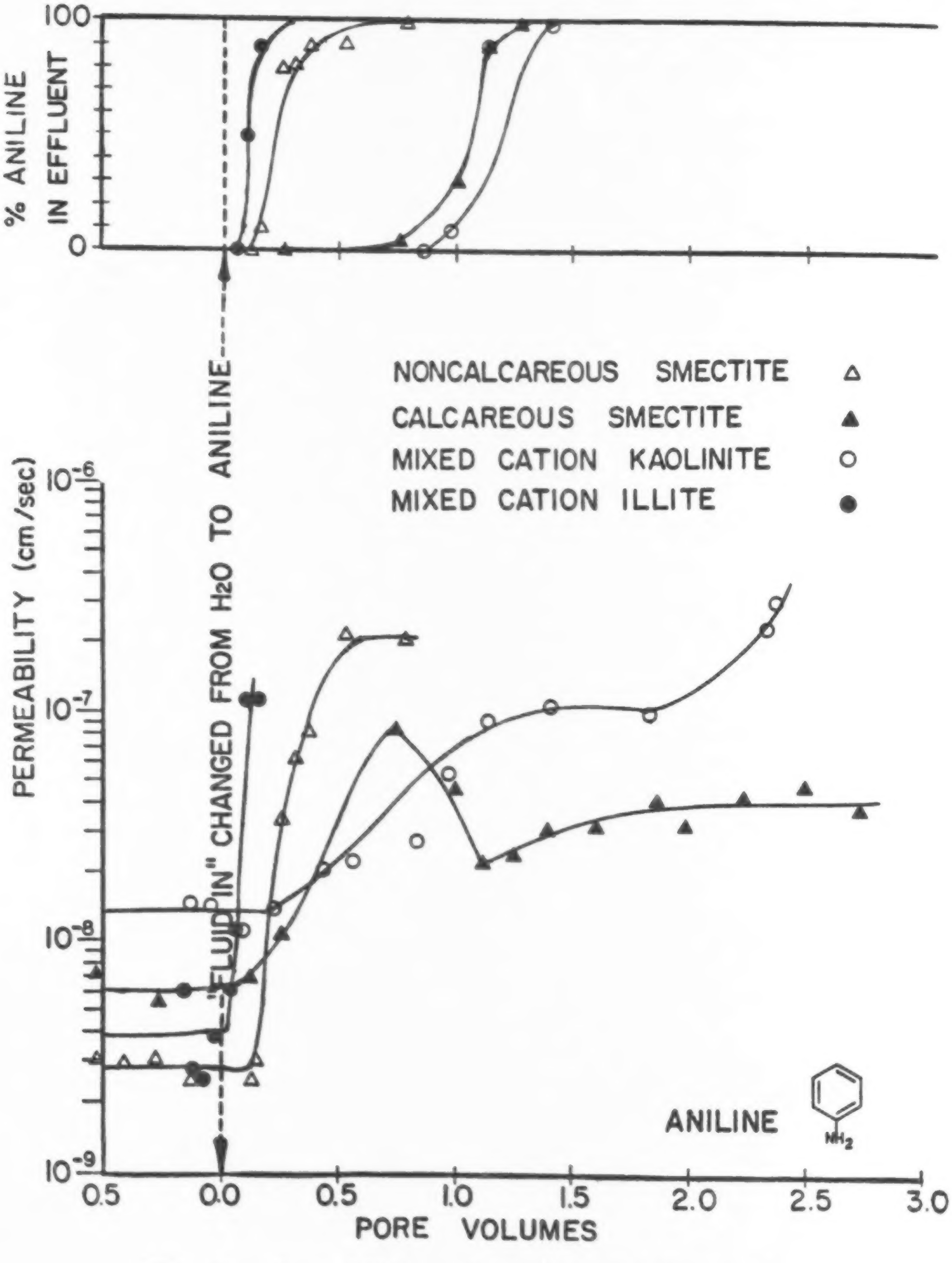

FIG. 24. Permeability and Breakthrough Curves of the Four Clay Soils Treated with Aniline

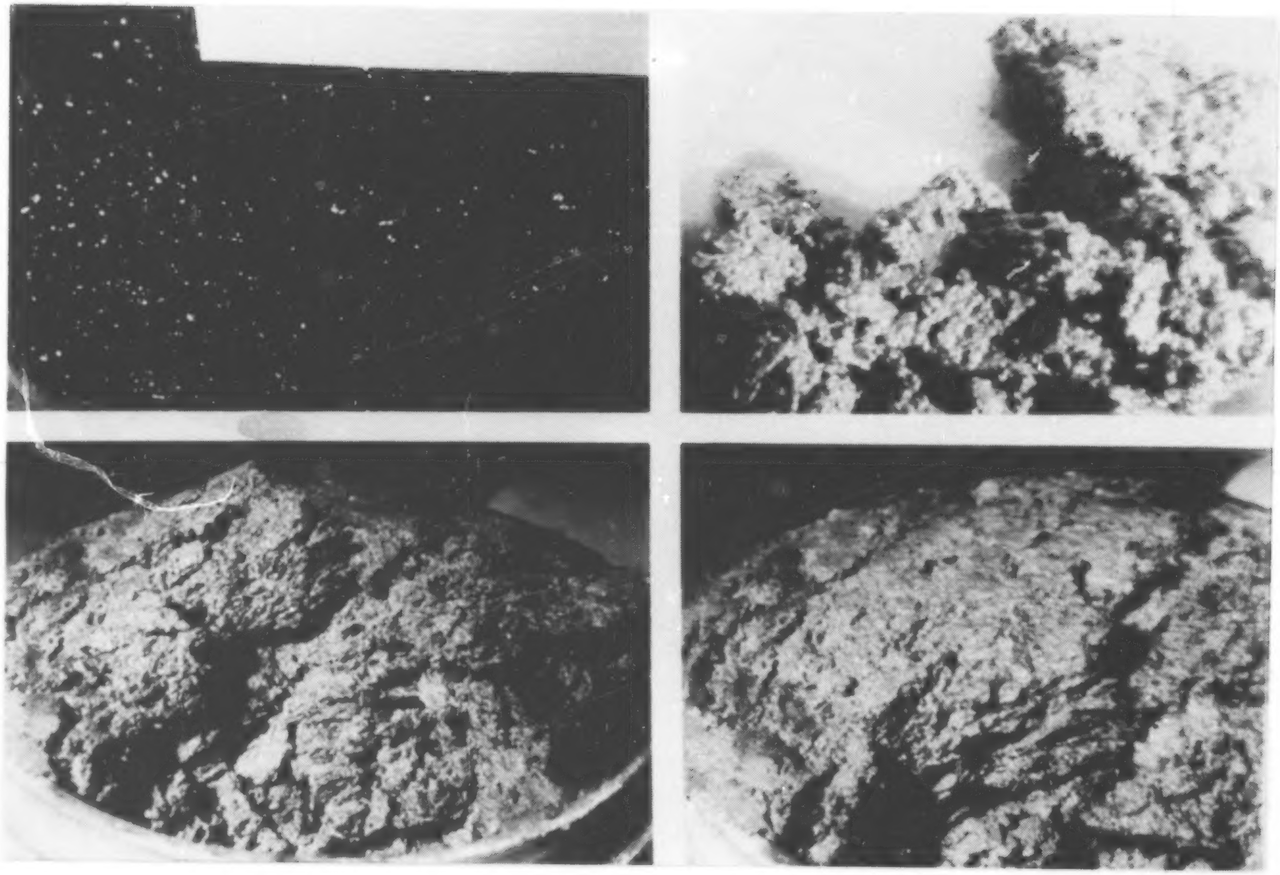

FIG. 25. Surface (upper left), Removed Soil (upper right), and the Soil Exposed after Core Excavation (lower two) of the Aniline-Treated Noncalcareous Smectitic Clay Soil

NEUTRAL POLAR ORGANICS

Ethylene Glycol

Permeabilities of the four clay soils to ethylene glycol are depicted in Fig. 26. As with aniline-treated cores, permeability trends with ethylene glycol showed little consistency with predicted intrinsic permeability values. The ratio of density to viscosity of ethylene glycol suggests that resulting soil permeability should be only 5% of that obtained with water. However, actual permeability values indicated that it was the ability of ethylene glycol to alter the soil fabric that was the dominating influence on permeability.

Three of the clay soils treated with ethylene glycol showed initial permeability decreases. The kaolinitic clay soil continued to undergo permeability decreases as long as it was being tested. The illitic clay soil began showing a permeability increase after passage of 0.5 pore volumes. In contrast, the calcareous smectite followed its initial permeability decrease with a substantial increase, a second decrease, and finally reached a nearly constant value that continued until the end of the test period. None of the three clays that showed initial permeability decreases ever reached permeabilities greater than 1×10^{-7} cm sec^{-1}.

The noncalcareous smectitic clay soil treated with ethylene glycol showed an initial rapid increase in permeability and a slower but continuous increase after passage of 0.5 pore volume. Its permeability exceeded 1×10^{-7} cm sec^{-1} after passage of two pore volumes.

Permeability trends in ethylene glycol treated cores emphasized the need to pass at least one pore volume of an organic leachate to determine if the fluid is likely to affect permeability of a prospective clay liner. In addition, if the permeability increases during the passage of the first pore volume, an additional pore volume should be passed through the core to determine the upper limit of the permeability increase.

Acetone

Permeabilities of the four clay soils to acetone are given in Fig. 27. Three of the acetone-treated soils reached permeabilities in excess of 1×10^{-7} cm sec^{-1} prior to the passage of one pore volume, while the calcareous smectitic soil exceeded this permeability within 1.5 pore volumes.

While density to viscosity ratio of acetone (2.4) indicates that permeability should increase 240% over values obtained with water, the observed permeability increases actually exceeded 1000% for the acetone-treated soils. The illitic and calcareous smectitic clay soils underwent 100 fold (10,000%) permeability increases, while the noncalcareous smectitic clay soil had a 1,000 fold increase.

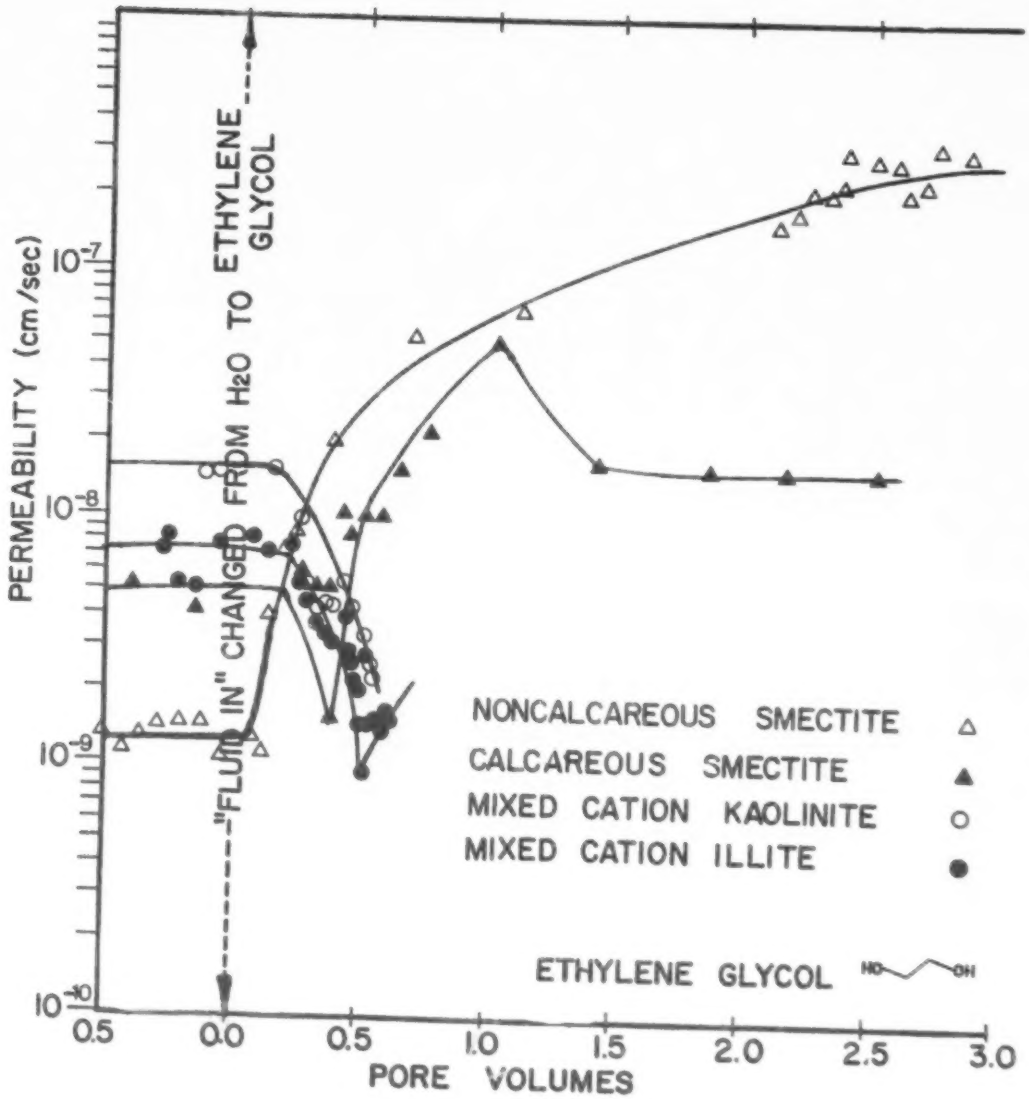

FIG. 26. Permeability of the Four Clay Soils to Ethylene Glycol

It is interesting to note that all soils treated with acetone had initial permeability decreases. These decreases continued until passage of approximately 0.5 pore volume. During passage of the next 0.5 pore volume, however, the soils underwent large permeability increases. One possible explanation for this sequence of permeability changes is as follows:

1. The higher dipole moment of acetone caused initial increase in interlayer spacing between adjacent clay particles as compared to water only.

2. As more acetone passed through the soil cores, more water layers were removed from clay surfaces. Due to its larger molecular weight, however, fewer acetone layers were adsorbed than had adsorbed when water was the only fluid present. This resulted in a larger effective cross-sectonal area available for fluid flow.

While acetone can displace water from clay surfaces due to its higher dipole moment, it cannot form as many adsorbed fluid layers as water due to its higher molecular weight.

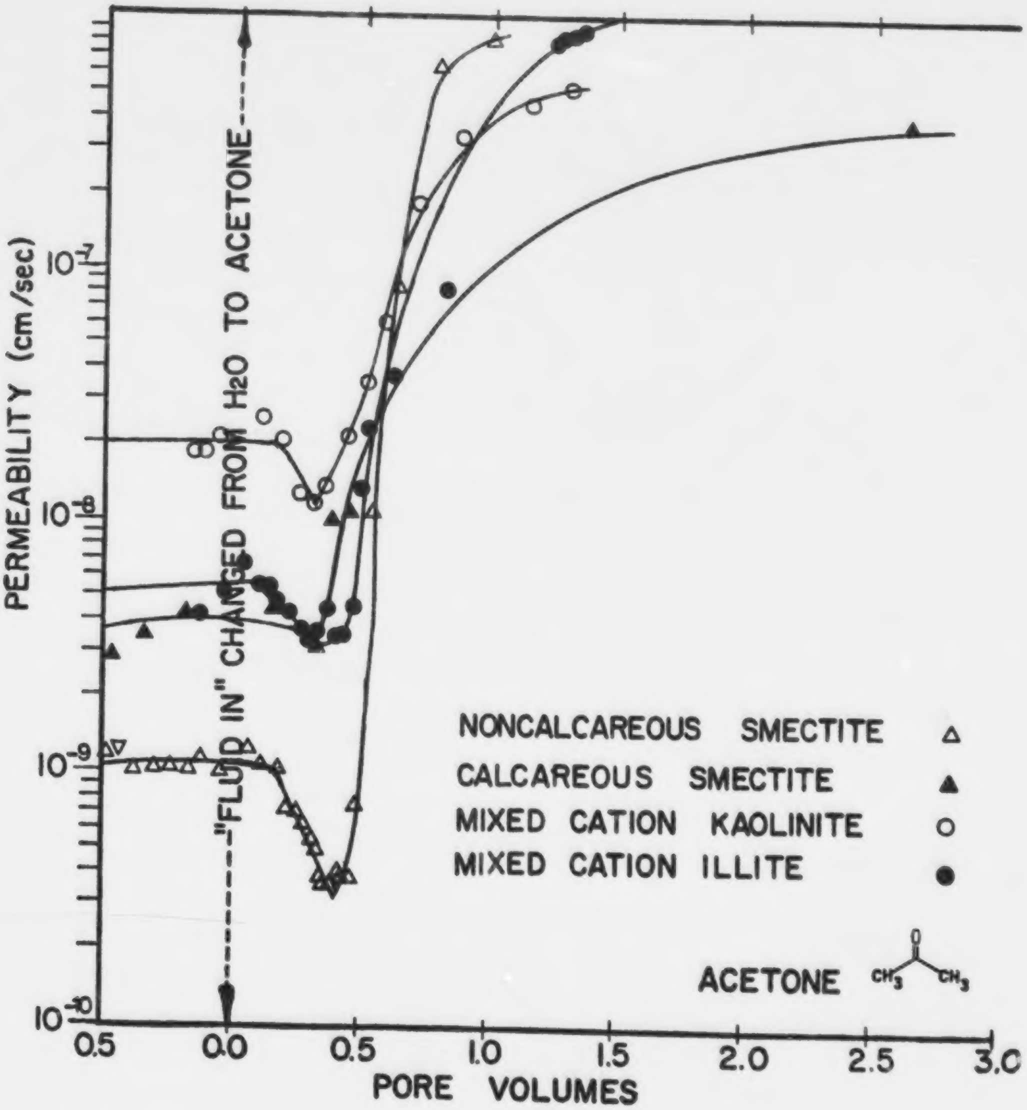

FIG. 27. Permeability of the Four Clay Soils to Acetone

In a previous study conducted by Green *et al*. (1981), this same initial decrease in permeability occurred with three other acetone-treated clay soils. Apparently, however, the tests were not of sufficient duration to pass enough of a pore volume to observe the large permeability increases as occurred in the present study above 0.5 pore volumes. This further illustrates the importance of passing at least one full pore volume of a waste leachate to determine how the fluid will affect the permeability of a clay liner.

Examination of the soil after acetone treatment showed extensive shrinkage and cracking. Such soil shrinkage is usually associated with dehydration, indicating that acetone had extracted water from soil particle surfaces.

Methanol

Permeabilities of the four soils treated with methanol and a breakthrough curve for the illitic clay soil are given in Fig. 28. As with acetone-treated soil cores, soil permeated with methanol reached permeabilities greater than 1 x 10^{-7} cm sec^{-1}. Unlike soils treated with acetone, methanol-treated soils underwent no initial permeability decrease.

Percent methanol in the effluent from the illitic clay soil paralleled an increase in permeability of the soil. After passage of 1.5 pore volumes, the hydraulic gradient was reduced from 61.1 to 1.85 and another pore volume of methanol passed (Fig. 29). Afer an initial decrease, permeability of the soil steadily increased at the lower hydraulic gradient to a value greater than 1 x 10^{-5} cm sec^{-1}.

No particle migration was detected in effluent from methanol-treated cores, and therefore soil piping was discounted as a mechanism for observed permeability increases. If these increases were due solely to the 1.46 density to viscosity ratio, permeability of the cores would have leveled at values 150% of those obtained with water. Instead, the cores showed steady permeability increases to values greater than 1,000% (kaolinitic soil) and 10,000% (illitic and noncalcareous soils) of permeability values with water.

Examination of methanol-treated soil cores revealed development of large pores and cracks visible on the soil surface (Fig. 30). The lower dielectric constant of methanol may have caused a decrease in interlayer spacing of the clay minerals present in the soils and thereby promoted the structural changes. Table 8 shows the trend relating dielectric constant to interlayer spacing for propanol, another low molecular weight alcohol, in various concentrations of water. In the case of propanol treated clay, it can be seen that both the dielectric constant of the fluid and the interlayer spacing of the clay decreased as the percentage propanol in the fluid increased.

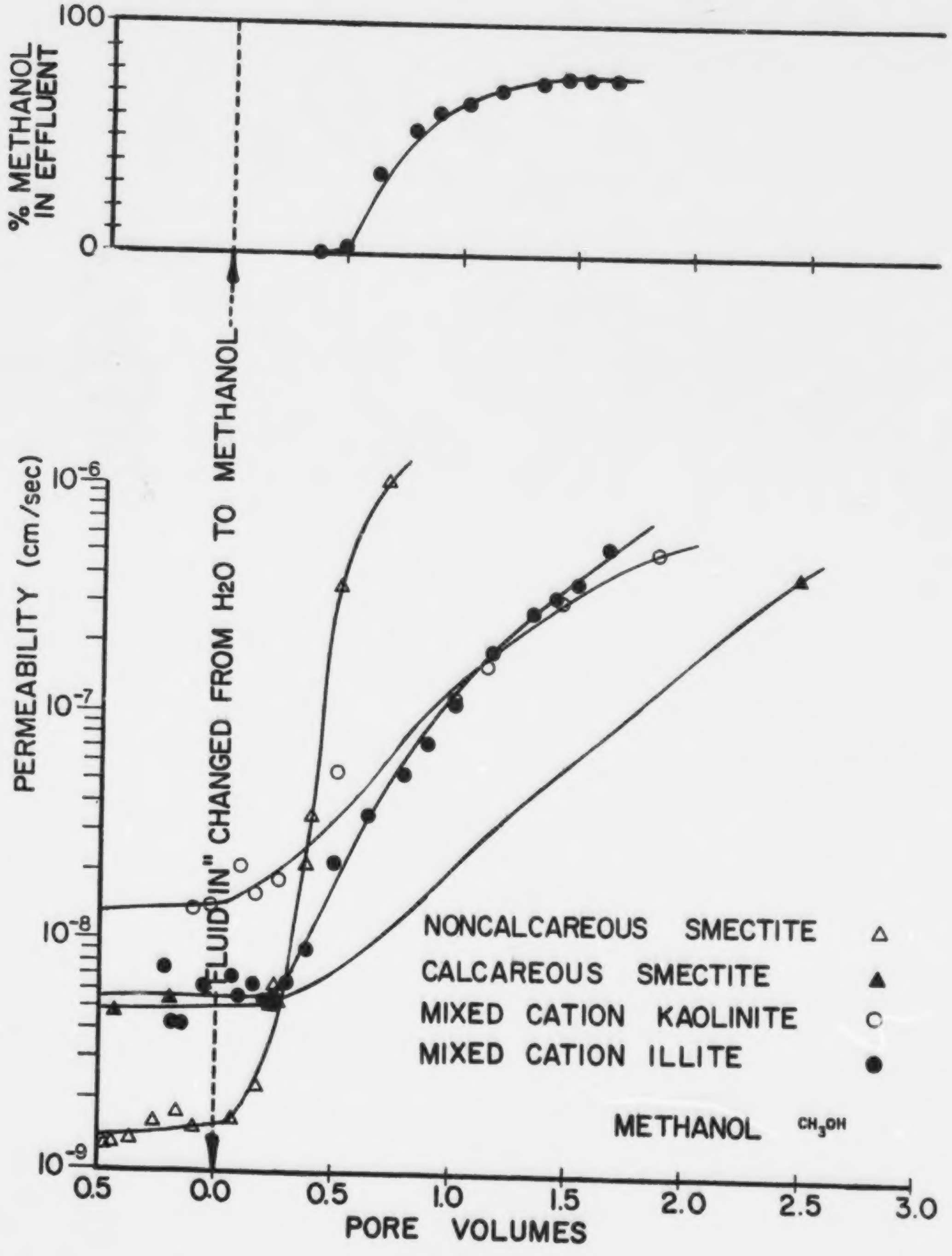

FIG. 28. Permeability of the Four Clay Soils to Methanol and the Breakthrough Curve for the Methanol-Treated Mixed Cation Illitic Clay Soil

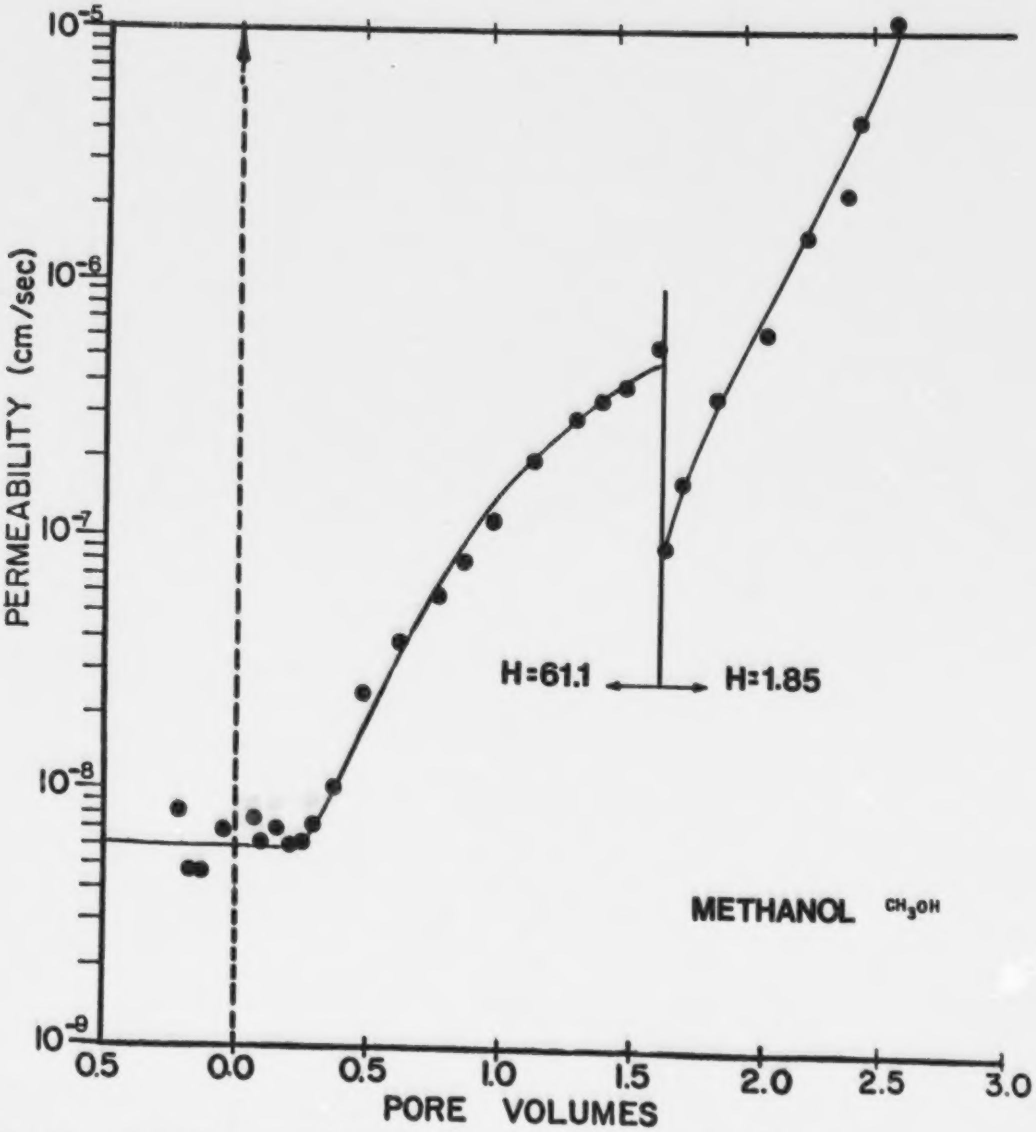

FIG. 29. Permeability of the Methanol-Treated Mixed Cation Illitic Clay Soil at Two Hydraulic Gradients

NEUTRAL NONPOLAR ORGANICS

Xylene

Permeabilities and breakthrough curves of the four clay soils treated with xylene are given in Fig. 31. Xylene-treated soils showed rapid

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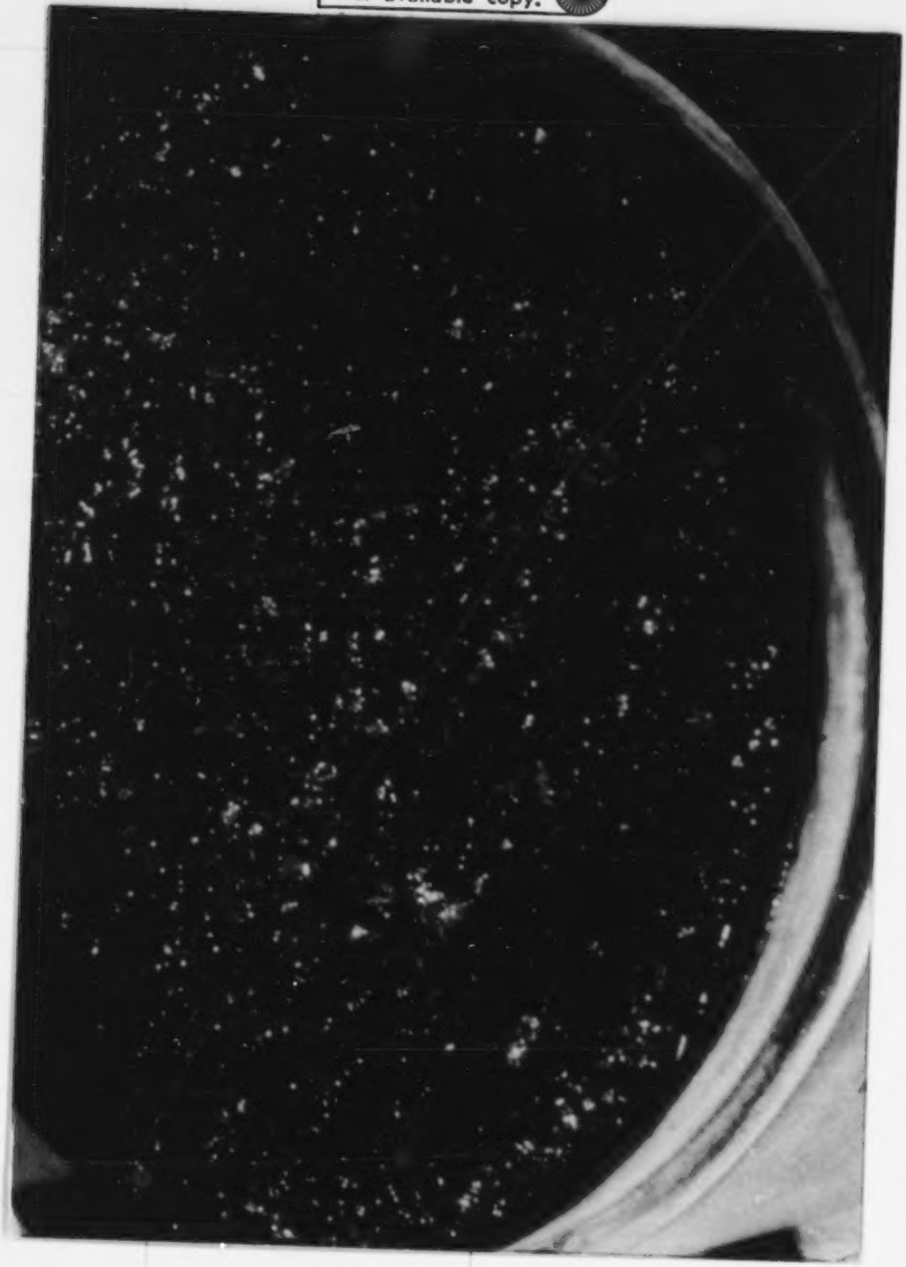

FIG. 30. Surface of the Methanol-Treated Noncalcareous Smectitic Clay Soil

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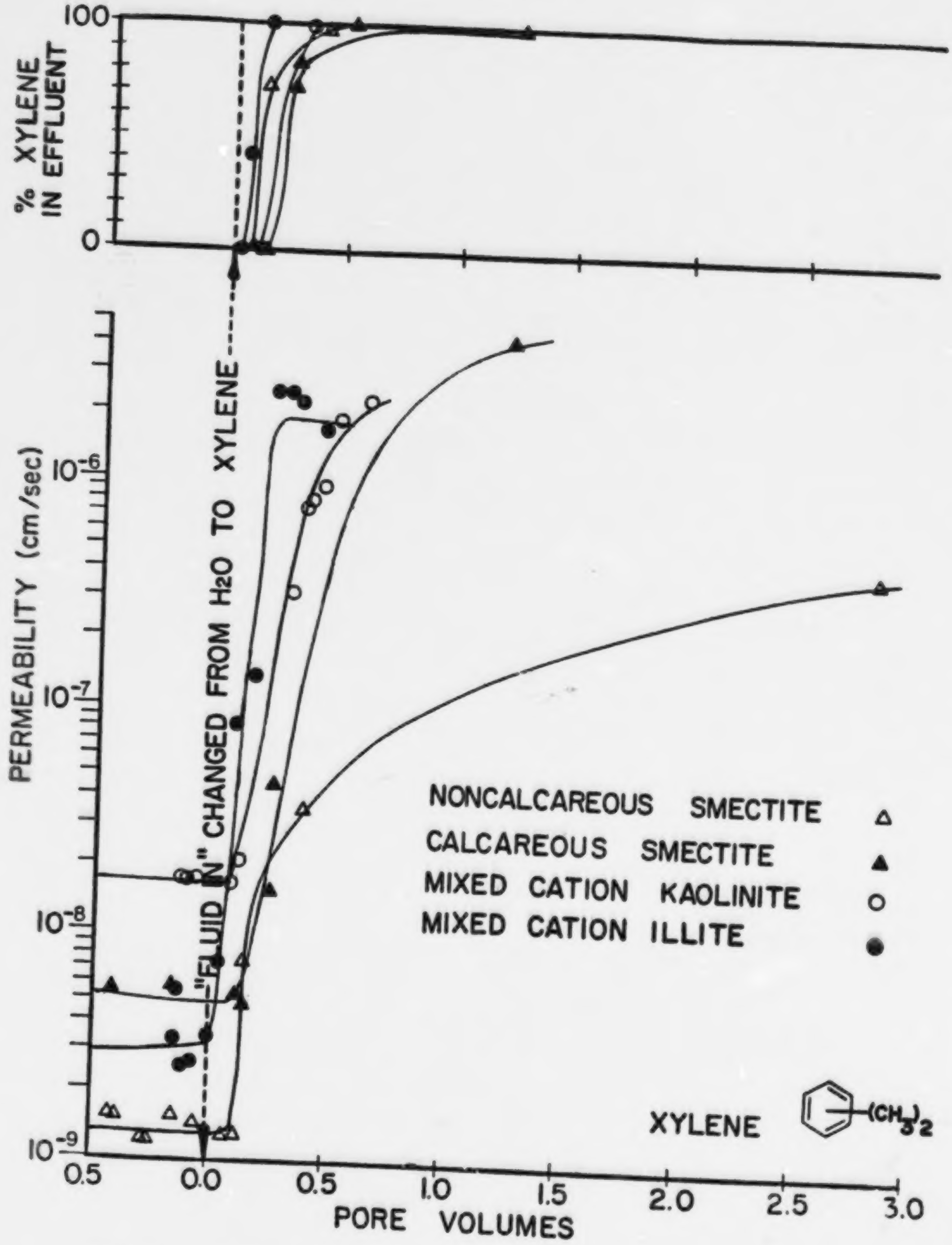

FIG. 31. Permeability and Breakthrough Curves of the Four Clay Soils Treated with Xylene

permeability increases followed by nearly constant permeabilities roughly two orders of magnitude greater than their permeabilities to water.

Permeability increases due to the ratio of density to viscosity of xylene (1.07) accounts for only a 7% increase in permeability over values obtained with water. Since permeability increases averaged 10,000% (two orders of magnitude), other mechanisms are obviously involved. An indication of these mechanisms was the structural changes in the xylene-treated soils, exemplified by massive structure before treatment and blocky structure after the soils were treated with xylene.

An earlier study by Green et al. (1981) noted that neutral nonpolar compounds such as xylene may greatly increase permeability of compacted clay soils by causing the formation of shrinkage cracks. This study however, erroneously listed the "equilibrium coefficient of permeability" for the xylene-treated soils as the low permeability values obtained prior to the formation of the shrinkage cracks. The authors compounded this error by plotting the artificially low permeability values for these neutral nonpolar fluids versus dielectric constant and arrived at the following conclusion: "All clay soils were more permeable to water than to organic solvents."

Heptane

Permeabilities and breakthrough curves of the four clay soils treated with heptane are given in Fig. 32. Premeability patterns for the heptane cores closely approximated those shown by the xylene treated cores. That is, the cores underwent initial permeability increases of roughly 10,000%. Following these initial large increases, rate of permeability increase slowed until nearly constant permeability values were observed.

Only the calcareous smectitic clay showed a significant difference in its permeability to the two neutral nonpolar liquids, with its permeability to heptane well below its permeability to xylene.

The constant permeability values eventually reached by the neutral nonpolar treated cores were probably related to the limited ability of these fluids to penetrate interlayer spaces of the clay minerals. Permeability trends for neutral nonpolar fluids differed from the continuous permeability increases observed in clay soils treated with neutral polar fluids, acetone and methanol.

REINTRODUCTION OF WATER

As stated earlier, changes in permeability for clay soils treated with organic fluids do not follow trends that would be predicted simply from changes in viscosity and density of the permeant fluid. Fig. 33 gives the permeability and breakthrough history of the noncalcareous smectitic clay

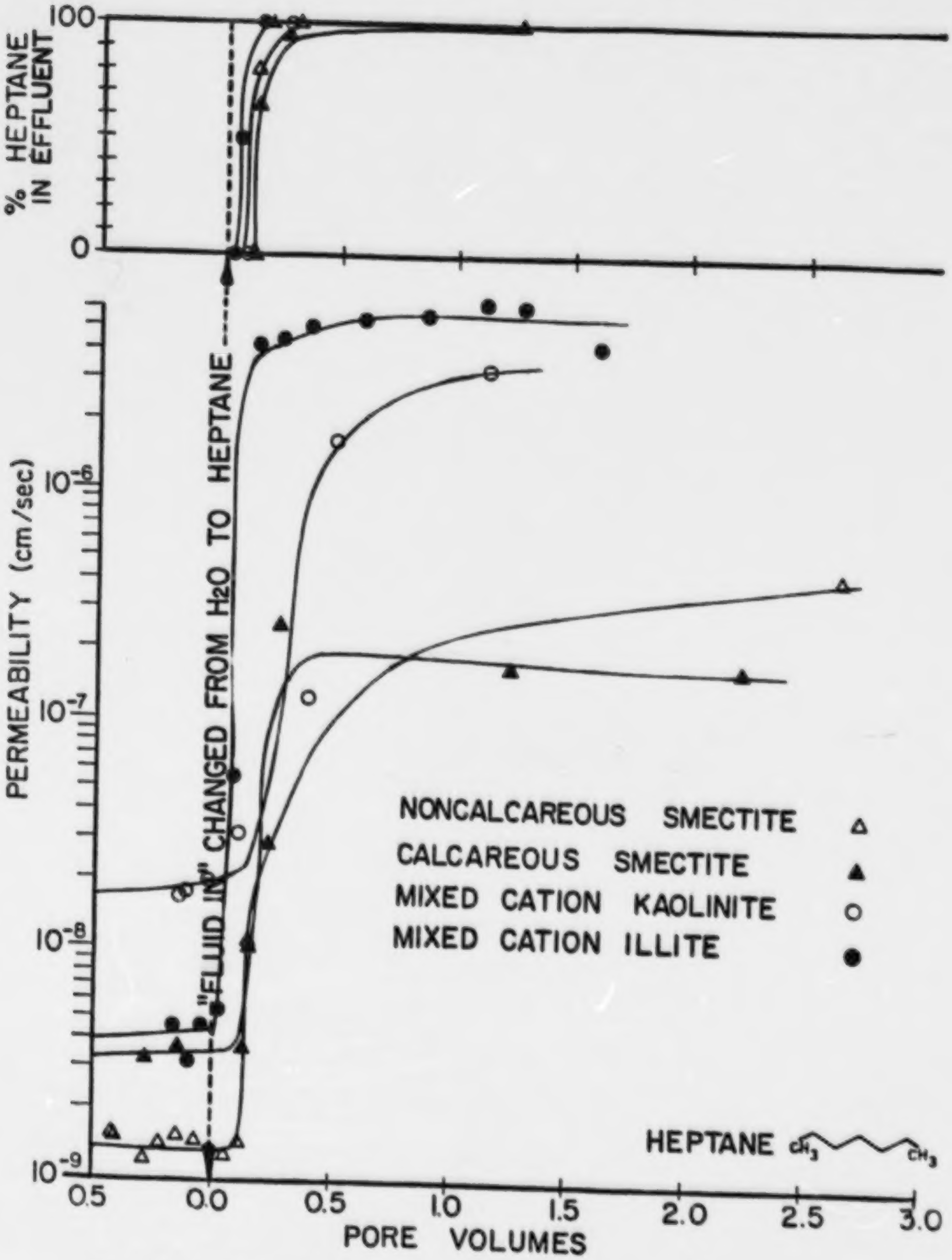

FIG. 32. Permeability and Breakthrough Curves of the Four Clay Soils Treated with Heptane

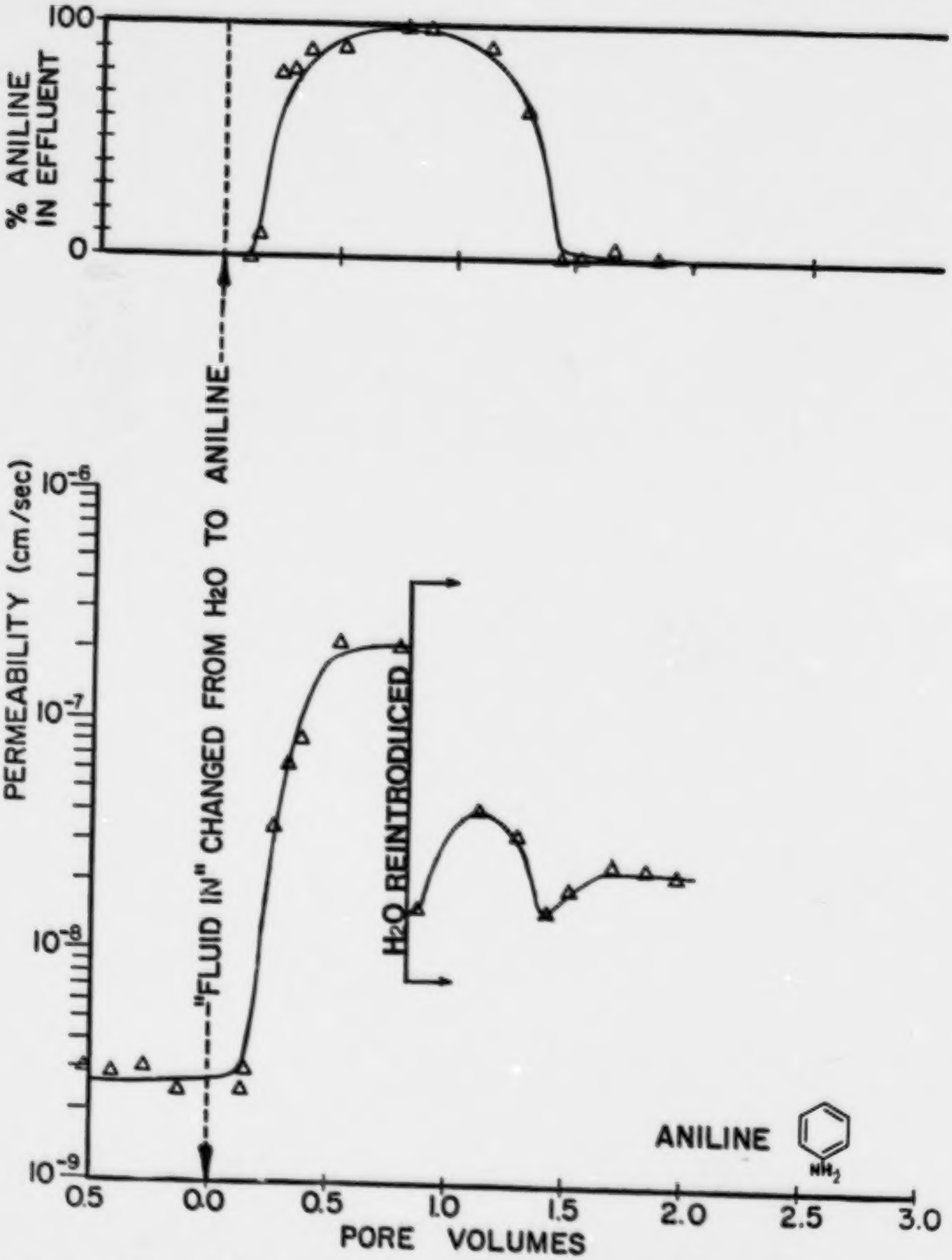

FIG. 33. Permeability and Breakthrough Curve for the Noncalcareous Smectitic Clay Soil Treated Sequentially with Water (0.01N $CaSO_4$), Aniline, and Water (0.01N $CaSO_4$)

soil sequentially permeated with water (0.01N $CaSO_4$), aniline, and water (0.01N $CaSO_4$).

According to intrinsic permeability theory, more viscous aniline should render the soil less permeable than water. In fact, the opposite trend was observed. Aniline increased permeability nearly two orders of magnitude. Reintroduction of water caused a subsequent decrease in the permeability of roughly one order of magnitude. Since reintroduction of water did not return the soil to its original permeability to water, there was at least partially irreversible structural alterations caused by the interaction of aniline with the compacted clay soil.

Water was also reintroduced on the noncalcareous smectitic clay soil after the soil had been treated with methanol and ethylene glycol (Table 17). The permeability trend (observed when water was reintroduced on the aniline-treated soil) also held for both the methanol and ethylene glycol-treated soils.

USE OF ELEVATED HYDRAULIC GRADIENTS

Two elevated gradients were used to shorten the time required for these permeability studies. A gradient of 361.6 was used with the smectitic clay soils and a gradient of 61.1 was used with both the illitic and kaolinitic clay soils. There were no signs of particle migration or turbulent flow in the neutral or basic organic fluid treated clay soils at either gradient. In addition, the gradients used did not appear to affect the permeability trend established by water or the organic fluids.

A disadvantage of using the higher gradient (361.6) was the rapidity with which permeability changes occurred. On several occasions, an

TABLE 17: PERMEABILITY OF NONCALCAREOUS SMECTITIC CLAY SOIL TO THE FOLLOWING FLUID SEQUENCE: WATER (0.01N $CaSO_4$)-TEST FLUID-WATER (0.01N $CaSO_4$)

Test Fluid	Initial Permeability to Water (0.01N $CaSO_4$) (cm sec^{-1})	Permeability to Test Fluid (cm sec^{-1})	Final Permeability to Water (0.01N $CaSO_4$) (cm sec^{-1})
Aniline	$2.91(\pm 0.23) \times 10^{-9}$	2.2×10^{-7}	2.3×10^{-8}
Methanol	$1.55(\pm 0.17) \times 10^{-9}$	1.1×10^{-6}	6.0×10^{-8}
Ethylene Glycol	$1.39(\pm 0.14) \times 10^{-9}$	3.1×10^{-7}	1.1×10^{-7}

increase occurred so quickly that the entire fluid reservoir was depleted before the end of a sampling period, thus permitting air to blow through and dehydrate the soil.

There were two main advantages of using the low hydraulic gradient (61.1). First, the lower gradient retained the advantage of a shortened testing time. Secondly, permeability changes at the lower gradient occurred slowly enough to obtain several points along a changing permeability curve.

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APPENDIX A

MOISTURE-DENSITY-PERMEABILITY RELATIONS DATA

TABLE A-1. MOISTURE-DENSITY-PERMEABILITY RELATIONS OF NONCALCAREOUS SMECTITE SOIL

Water Content (% of Dry Density)	Dry Density (kNm^{-3})	Permeability (cm sec^{-1})
14.1	13.7	1.55×10^{-7}
16.6	14.2	2.51×10^{-8}
17.8	14.8	ND
20.0	15.0	1.50×10^{-9}
21.7	14.7	2.54×10^{-9}
21.8	14.6	ND

ND - not determined.

TABLE A-2. MOISTURE-DENSITY-PERMEABILITY RELATIONS OF CALCAREOUS SMECTITE SOIL

Water Content (% of Dry Density)	Dry Density (kNm^{-3})	Permeability (cm sec^{-1})
15.9	12.1	7.00×10^{-6}
16.4	12.6	ND
18.0	13.3	1.75×10^{-6}
20.0	13.5	2.13×10^{-7}
20.7	14.5	ND
22.1	14.4	6.13×10^{-8}
22.6	14.4	ND
23.3	13.7	5.24×10^{-9}
23.5	14.1	4.49×10^{-9}

ND - not determined.

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TABLE A-3. MOISTURE-DENSITY-PERMEABILITY RELATIONS OF MIXED CATION OF KAOLINITE SOIL

Water Content (% of Dry Density)	Dry Density (kNm^{-3})	Permeability (cm sec^{-1})
16.2	15.7	6.23×10^{-6}
18.8	16.4	4.39×10^{-8}
21.7	16.0	1.78×10^{-8}
21.7	16.2	1.98×10^{-8}
22.0	16.1	1.32×10^{-8}
22.3	15.7	2.06×10^{-8}
23.9	15.4	1.70×10^{-7}
24.6	15.2	2.61×10^{-7}

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TABLE A-4. MOISTURE-DENSITY-PERMEABILITY RELATIONS OF ILLITE SOIL

Water Content (% of Dry Density)	Dry Density (kNm^{-3})	Permeability ($cm\ sec^{-1}$)
15.6	16.4	8.83×10^{-8}
17.3	16.5	5.23×10^{-8}
19.0	16.6	6.94×10^{-9}
20.2	16.5	5.03×10^{-9}
22.1	16.5	ND
24.7	15.6	3.55×10^{-9}
25.2	15.4	3.49×10^{-9}
26.5	15.1	4.88×10^{-9}

ND - not determined.

APPENDIX B

PHYSICAL DATA ON THE SOIL COLUMNS USED IN THE STUDY

TABLE B-1. DATA ON THE NONCALCAREOUS SMECTITE SOIL COLUMNS PREPARED FOR THE PERMEABILITY STUDIES

Compaction Water Content (% dry density)	Dry Density Before Swelling (kNm^{-3})	Dry Density After Swelling (kNm^{-3})	% Swelling	Porosity After Swelling	Pore Volume After Swelling (cm^3)
21.7	14.7	14.7	4	0.444	416
20.0	15.0	14.4	4	0.432	405
20.0	14.9	14.3	4	0.437	409
20.0	14.8	14.4	3	0.434	407
21.5	14.6	14.0	4	0.448	419
21.5	15.3	14.6	5	0.426	399
21.5	15.1	14.5	4	0.428	401
21.7	14.8	14.2	4	0.439	411

TABLE B-2. DATA ON THE CALCAREOUS SMECTITE SOIL COLUMNS PREPARED FOR THE PERMEABILITY STUDIES

Compaction Water Content (% dry density)	Dry Density Before Swelling (kNm^{-3})	Dry Density After Swelling (kNm^{-3})	% Swelling	Porosity After Swelling	Pore Volume After Swelling (cm^3)
23.3	13.5	12.5	7	0.502	471
23.5	14.0	13.2	6	0.473	443
23.3	13.6	12.8	6	0.488	457
23.3	14.1	13.0	8	0.478	448
23.3	13.7	12.7	7	0.493	462
23.5	14.0	12.9	8	0.486	455
23.5	14.0	12.9	8	0.485	454
23.3	13.3	12.3	8	0.510	478

TABLE B-3. DATA ON THE MIXED CATION KAOLINITE SOIL COLUMNS PREPARED FOR THE PERMEABILITY STUDIES

Compaction Water Content (% dry density)	Dry Density Before Swelling (kNm^{-3})	Dry Density After Swelling (kNm^{-3})	% Swelling	Porosity After Swelling	Pore Volume After Swelling (cm^3)
22.3	15.7	15.7	0	0.418	395
21.7	16.1	16.1	0	0.400	378
21.7	16.0	16.0	0	0.407	385
22.0	16.1	16.1	0	0.404	381
22.2	15.7	15.7	0	0.418	395
22.3	15.3	15.3	0	0.433	409
21.7	15.7	15.7	0	0.418	395
22.1	15.4	15.4	0	0.429	405

TABLE B-4. DATA ON THE MIXED CATION ILLITE SOIL COLUMNS PREPARED FOR THE PERMEABILITY STUDIES

Compaction Water Content (% dry density)	Dry Density Before Swelling (kNm^{-3})	Dry Density After Swelling (kNm^{-3})	% Swelling	Porosity After Swelling	Pore Volume After Swelling (cm^3)
25.1	15.6	15.2	2.5	0.425	398
26.5	15.1	14.8	2.1	0.441	413
25.2	15.4	15.0	2.5	0.432	405
25.6	15.4	15.0	2.3	0.432	405
26.9	15.4	15.1	2.0	0.430	402
24.7	15.6	15.2	2.6	0.426	339
25.4	15.6	15.0	2.4	0.435	408
24.8	15.5	15.1	2.6	0.431	404

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APPENDIX C

PERMEABILITY DATA ON THE SOIL COLUMNS USED IN THE STUDY

TABLE C-1. PERMEABILITY HISTORY FOR THE NONCALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) (CONTROL)
(PORE VOLUME = 416 cm^3; HYDRAULIC GRADIENT = 361.6)

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
2.15×10^{-9}	6.912×10^5	43.0	0.51
1.97×10^{-9}	6.912×10^5	39.5	0.41
1.80×10^{-9}	6.912×10^5	36.0	0.32
2.40×10^{-9}	6.912×10^5	48.0	0.23
2.37×10^{-9}	6.912×10^5	47.5	0.11
"Fluid In" continued with H_2O (0.01N $CaSO_4$)			0.0
1.97×10^{-9}	6.912×10^5	39.5	0.09
2.00×10^{-9}	6.912×10^5	40.0	0.19
2.00×10^{-9}	6.912×10^5	40.0	0.29
2.42×10^{-9}	6.912×10^5	48.5	0.40
2.35×10^{-9}	6.912×10^5	47.0	0.52
2.50×10^{-9}	6.912×10^5	50.0	0.64
2.32×10^{-9}	6.912×10^5	46.5	0.75
2.50×10^{-9}	6.912×10^5	50.0	0.87
2.52×10^{-9}	6.912×10^5	50.5	0.99
2.55×10^{-9}	6.912×10^5	51.0	1.11
2.45×10^{-9}	6.912×10^5	49.0	1.23
2.62×10^{-9}	6.912×10^5	52.5	1.36
2.45×10^{-9}	6.912×10^5	49.0	1.47

TABLE C-2. PERMEABILITY HISTORY FOR THE NONCALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ACETIC ACID

(PORE VOLUME = 407 cm^3; HYDRAULIC GRADIENT = 361.6)

K ($cm\ sec^{-1}$)	T (sec)	Volume (mls)	Pore Volume
1.65×10^{-9}	6.912×10^5	33.0	0.47
1.92×10^{-9}	6.912×10^5	38.5	0.39
1.65×10^{-9}	6.912×10^5	33.0	0.29
1.45×10^{-9}	6.912×10^5	29.0	0.21
1.52×10^{-9}	6.912×10^5	30.5	0.14
1.37×10^{-9}	6.912×10^5	27.5	0.07
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Acetic Acid			0.0
1.75×10^{-9}	6.912×10^5	35.0	0.09
1.37×10^{-9}	6.912×10^5	27.5	0.15
1.02×10^{-9}	6.912×10^5	20.5	0.20
6.50×10^{-10}	6.912×10^5	13.0	0.24
4.75×10^{-10}	1.382×10^6	19.0	0.28
3.87×10^{-10}	1.382×10^6	15.5	0.32
4.62×10^{-10}	1.382×10^6	18.5	0.37
4.25×10^{-10}	1.382×10^6	17.0	0.41
2.62×10^{-10}	1.382×10^6	10.5	0.43
1.96×10^{-9}	1.382×10^6	78.5	0.63
2.77×10^{-9}	1.382×10^6	111.0	0.90
6.26×10^{-9}	1.382×10^6	250.5	1.51
9.85×10^{-9}	1.037×10^6	296.0	2.24

TABLE C-3. PERMEABILITY HISTORY FOR THE NONCALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ANILINE (PORE VOLUME = 419 cm^3; HYDRAULIC GRADIENT = 361.6)

Effluent H_2O(%)	Effluent Aniline(%)	K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
100	0	3.00×10^{-9}	6.912×10^5	60.0	0.55
100	0	2.95×10^{-9}	6.912×10^5	59.0	0.41
100	0	3.10×10^{-9}	6.912×10^5	62.0	0.27
100	0	2.57×10^{-9}	6.912×10^5	51.5	0.12
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Aniline					0.0
100	0	2.52×10^{-9}	6.912×10^5	50.5	0.12
∿87	∿13	3.00×10^{-9}	8.64×10^4	7.5	0.14
∿19	∿81	3.41×10^{-8}	4.50×10^4	44.5	0.24
∿16	∿84	6.64×10^{-8}	1.17×10^4	22.5	0.30
∿10	∿90	8.94×10^{-8}	1.158×10^4	30.0	0.37
<10	>90	2.28×10^{-7}	1.135×10^4	75.0	0.55
Trace	∿100	2.17×10^{-7}	1.638×10^4	103.0	0.79
Water (0.01N $CaSO_4$) reintroduced as the "Fluid In"					(0.0)
Trace	∿100	1.60×10^{-8}	8.64×10^4	40.0	0.89(0.10)
∿9	∿91	4.22×10^{-8}	8.64×10^4	105.5	1.14(0.35)
∿35	∿65	3.20×10^{-8}	8.64×10^4	80.0	1.33(0.54)
∿100	Trace	1.56×10^{-8}	8.64×10^4	39.0	1.43(0.63)
∿100	Trace	1.96×10^{-8}	8.64×10^4	49.0	1.54(0.75)
∿4	∿96	2.50×10^{-8}	8.64×10^4	62.5	1.69(0.90)
∿100	Trace	2.40×10^{-8}	8.64×10^4	60.0	1.84(1.04)
∿100	Trace	2.28×10^{-8}	8.64×10^4	57.0	1.97(1.18)

TABLE C-4. PERMEABILITY HISTORY FOR THE NONCALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ETHYLENE GLYCOL

(PORE VOLUME = 411 cm^3; HYDRAULIC GRADIENT = 361.6)

K ($cm\ sec^{-1}$)	T (sec)	Volume (mls)	Pore Volume
1.42×10^{-9}	1.382×10^{6}	57.0	0.54
1.22×10^{-9}	6.912×10^{5}	24.5.	0.41
1.40×10^{-9}	6.912×10^{5}	28.0	0.35
1.50×10^{-9}	6.912×10^{5}	30.0	0.28
1.52×10^{-9}	6.912×10^{5}	30.5	0.20
1.52×10^{-9}	6.912×10^{5}	30.5	0.13
1.17×10^{-9}	6.912×10^{5}	23.5	0.06
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Ethylene Glycol			0.0
1.40×10^{-9}	6.912×10^{5}	28.0	0.07
1.20×10^{-9}	3.456×10^{5}	12.0	0.10
4.00×10^{-9}	8.64×10^{4}	10.0	0.12
7.59×10^{-9}	8.64×10^{4}	19.0	0.17
8.79×10^{-9}	8.64×10^{4}	22.0	0.22
2.08×10^{-8}	8.64×10^{4}	52.0	0.35
5.51×10^{-8}	8.64×10^{4}	138.0	0.68
6.87×10^{-8}	8.64×10^{4}	172.0	1.10
1.68×10^{-7}	8.64×10^{4}	420.0	2.12
1.80×10^{-7}	4.80×10^{3}	25.0	2.18
2.24×10^{-7}	3.84×10^{3}	25.0	2.24
2.15×10^{-7}	3.54×10^{3}	22.0	2.29

(Continued)

TABLE C-4. CONTINUED

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
2.40×10^{-8}	1.32×10^{3}	9.0	2.32
3.07×10^{-7}	3.60×10^{3}	32.0	2.40
2.92×10^{-7}	3.30×10^{3}	28.0	2.46
2.88×10^{-7}	1.56×10^{3}	13.0	2.50
2.04×10^{-7}	4.74×10^{3}	28.0	2.56
2.47×10^{-7}	3.90×10^{3}	28.0	2.63
3.19×10^{-7}	2.88×10^{3}	26.0	2.70
3.07×10^{-7}	3.60×10^{3}	32.0	2.78

TABLE C-5. PERMEABILITY HISTORY FOR THE NONCALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ACETONE (PORE VOLUME = 399 cm^3; HYDRAULIC GRADIENT = 361.6)

K ($cm\ sec^{-1}$)	T (sec)	Volume (mls)	Pore Volume
1.29×10^{-9}	1.382×10^6	51.5	0.46
1.02×10^{-9}	6.912×10^5	20.5	0.34
1.15×10^{-9}	6.912×10^5	23.0	0.28
1.15×10^{-9}	6.912×10^5	23.0	0.23
1.10×10^{-9}	6.912×10^5	22.0	0.17
1.25×10^{-9}	6.912×10^5	25.0	0.11
1.02×10^{-9}	6.912×10^5	20.5	0.05
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Acetone			0.0
1.30×10^{-9}	6.912×10^5	26.0	0.06
1.12×10^{-9}	6.912×10^5	22.5	0.12
1.10×10^{-9}	6.912×10^5	22.0	0.18
7.49×10^{-10}	6.912×10^5	15.0	0.21
7.24×10^{-10}	6.912×10^5	14.5	0.25
6.49×10^{-10}	6.912×10^5	13.0	0.28
5.49×10^{-10}	6.912×10^5	11.0	0.31
4.99×10^{-10}	6.912×10^5	10.0	0.34
4.00×10^{-10}	6.912×10^5	8.0	0.36
3.75×10^{-10}	6.912×10^5	7.5	0.37
$3.75 \times \times 10^{-10}$	6.912×10^5	7.5	0.39
4.24×10^{-10}	6.912×10^5	8.5	0.41

(Continued)

TABLE C-5. CONTINUED

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
4.00×10^{-10}	6.912×10^{5}	8.0	0.43
4.00×10^{-10}	6.912×10^{5}	8.0	0.45
7.66×10^{-10}	5.184×10^{5}	11.5	0.48
1.12×10^{-8}	8.640×10^{4}	28.0	0.55
8.95×10^{-8}	1.080×10^{4}	28.0	0.62
6.71×10^{-7}	3.600×10^{3}	70.0	0.80
8.06×10^{-7}	3.600×10^{3}	84.0	1.01

TABLE C-6. PERMEABILITY HISTORY FOR THE NONCALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY METHANOL (PORE VOLUME = 401 cm^3; HYDRAULIC GRADIENT = 361.6)

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
1.37×10^{-9}	6.912×10^5	27.5	0.46
1.40×10^{-9}	6.912×10^5	28.0	0.40
1.47×10^{-9}	6.912×10^5	29.5	0.32
1.65×10^{-9}	6.912×10^5	33.0	0.25
1.82×10^{-9}	6.912×10^5	36.5	0.17
1.57×10^{-9}	6.912×10^5	31.5	0.08
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Methanol			0.0
1.72×10^{-9}	6.912×10^5	34.5	0.09
2.31×10^{-9}	6.048×10^5	40.5	0.19
6.79×10^{-9}	8.640×10^4	17.0	0.23
2.18×10^{-8}	8.640×10^4	54.5	0.36
3.84×10^{-8}	4.500×10^3	5.0	0.38
3.66×10^{-7}	4.200×10^3	44.5	0.49
1.12×10^{-6}	2.580×10^3	84.0	0.70

TABLE C-7. PERMEABILITY HISTORY FOR THE NONCALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY XYLENE (PORE VOLUME = 409 cm^3; HYDRAULIC GRADIENT = 361.6)

Effluent		K	T	Volume	Pore
H_2O(%)	Xylene(%)	(cm sec^{-1})	(sec)	(mls)	Volume
100	0	1.63×10^{-9}	5.184×10^{5}	24.5	0.40
100	0	1.55×10^{-9}	6.912×10^{5}	31.0	0.34
100	0	1.20×10^{-9}	6.912×10^{5}	24.0	0.27
100	0	1.17×10^{-9}	6.912×10^{5}	23.5	0.21
100	0	1.62×10^{-9}	6.912×10^{5}	32.5	0.15
100	0	1.47×10^{-9}	6.912×10^{5}	29.5	0.07
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Xylene					0.0
100	0	1.30×10^{-9}	6.912×10^{5}	26.0	0.06
100	0	1.34×10^{-9}	6.048×10^{5}	23.5	0.12
∿26	∿74	7.59×10^{-9}	8.640×10^{4}	19.0	0.17
∿1	∿99	3.56×10^{-8}	8.640×10^{4}	89.0	0.38
Trace	∿100	$>4.00 \times 10^{-7}$	8.640×10^{4}	>1000*	>2.82

* Entire volume of the fluid chanber (∿1 liter) was released within one sampling period (24 hrs) resulting in air blowing through the core.

TABLE C-8. PERMEABILITY HISTORY FOR THE NONCALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY HEPTANE (PORE VOLUME = 405 cm^3; HYDRAULIC GRADIENT = 361.6)

Effluent		K	T	Volume	Pore
H_2O(%)	Heptane(%)	(cm sec^{-1})	(sec)	(mls)	Volume
100	0	1.62×10^{-9}	6.912×10^5	32.5	0.43
100	0	1.57×10^{-9}	6.912×10^5	31.0	0.35
100	0	1.27×10^{-9}	6.912×10^5	25.5	0.27
100	0	1.47×10^{-9}	6.912×10^5	29.5	0.21
100	0	1.60×10^{-9}	6.912×10^5	32.0	0.13
100	0	1.50×10^{-9}	5.184×10^5	22.5	0.06
"Fluid In" changed from H_2O (0.01N $CaSO_4$) Heptane					0.0
100	0	1.33×10^{-9}	5.184×10^5	20.0	0.05
100	0	1.50×10^{-9}	6.912×10^5	30.0	0.12
∿18	∿82	1.08×10^{-8}	8.640×10^4	27.0	0.19
Trace	∿100	$>4.00 \times 10^{-7}$	8.640×10^4	1000*	>2.65

* Entire volume of the fluid chamber (∿1 liter) was released within one sampling period (24 hrs) resulting in air blowing through the core.

TABLE C-9. PERMEABILITY HISTORY FOR THE CALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) (CONTROL)

(PORE VOLUME = 471 cm^3; HYDRAULIC GRADIENT = 361.6)

K ($cm\ sec^{-1}$)	T (sec)	Volume (mls)	Pore Volume
7.32×10^{-9}	5.184×10^5	110.0	0.50
8.22×10^{-9}	5.184×10^5	123.5	0.26
"Fluid In" continued with H_2O (0.01N $CaSO_4$)			0.0
8.94×10^{-9}	6.912×10^5	179.0	0.38
7.27×10^{-9}	6.912×10^5	145.5	0.69
7.47×10^{-9}	6.912×10^5	149.5	1.01
6.49×10^{-9}	6.912×10^5	130.0	1.28
5.77×10^{-9}	6.912×10^5	115.5	1.53
5.42×10^{-9}	6.912×10^5	108.5	1.76

TABLE C-10. PERMEABILITY HISTORY FOR THE CALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ANILINE (PORE VOLUME = 454 cm^3; HYDRAULIC GRADIENT = 361.6)

Effluent H_2O(%)	Effluent Aniline(%)	K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
100	0	7.29×10^{-9}	6.912×10^4	146.0	0.56
100	0	5.67×10^{-9}	6.912×10^4	113.5	0.24
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Aniline					0.0
100	0	7.04×10^{-9}	3.456×10^4	70.5	0.15
100	0	1.12×10^{-8}	1.728×10^4	56.0	0.27
∿96	∿4	8.63×10^{-8}	8.640×10^4	216.0	0.74
∿90	∿30	4.80×10^{-8}	8.640×10^4	120.0	1.00
<10	>90	2.32×10^{-8}	8.640×10^4	58.0	1.13
Trace	∿100	2.52×10^{-8}	8.640×10^4	63.0	1.26
Trace	∿100	3.08×10^{-8}	8.640×10^4	77.0	1.43
Trace	∿100	3.28×10^{-8}	8.640×10^4	82.0	1.61
Trace	∿100	4.12×10^{-8}	8.640×10^4	103.0	1.83
Trace	∿100	3.36×10^{-8}	8.640×10^4	84.0	2.01
Trace	∿100	4.60×10^{-8}	8.640×10^4	115.0	2.26
Trace	∿100	4.96×10^{-8}	8.640×10^4	124.0	2.53
Trace	∿100	3.96×10^{-8}	8.640×10^4	99.0	2.74

TABLE C-11. PERMEABILITY HISTORY FOR THE CALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ACETIC ACID

(PORE VOLUME = 448 cm^3; HYDRAULIC GRADIENT = 361.6)

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
2.52×10^{-9}	6.912×10^5	50.5	0.29
5.19×10^{-9}	5.184×10^5	78.0	0.17
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Acetic Acid			0.0
4.64×10^{-9}	6.912×10^5	93.0	0.21
1.57×10^{-9}	6.912×10^5	31.5	0.28
8.74×10^{-10}	6.912×10^5	17.5	0.32
4.50×10^{-10}	6.912×10^5	9.0	0.34
2.00×10^{-10}	6.912×10^5	4.0	0.34
9.99×10^{-11}	1.037×10^6	3.0	0.35
4.99×10^{-11}	6.912×10^5	1.0	0.35

TABLE C-12. PERMEABILITY HISTORY FOR THE CALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ETHYLENE GLYCOL

(PORE VOLUME = 478 cm^3; HYDRAULIC GRADIENT = 361.6)

K ($cm\ sec^{-1}$)	T (sec)	Volume (mls)	Pore Volume
5.12×10^{-9}	6.912×10^5	102.5	0.39
4.22×10^{-9}	6.912×10^5	84.5	0.18
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Ethylene Glycol			0.0
6.07×10^{-9}	6.912×10^5	121.5	0.25
5.29×10^{-9}	1.728×10^5	26.5	0.31
5.39×10^{-9}	8.640×10^4	13.5	0.34
1.60×10^{-9}	8.640×10^4	4.0	0.35
1.08×10^{-8}	8.640×10^4	27.0	0.40
8.79×10^{-9}	8.640×10^4	22.0	0.45
1.12×10^{-8}	8.640×10^4	28.0	0.51
1.12×10^{-8}	8.640×10^4	28.0	0.56
1.64×10^{-8}	8.640×10^4	41.0	0.65
2.32×10^{-8}	8.640×10^4	58.0	0.77
5.27×10^{-8}	8.640×10^4	132.0	1.05
1.86×10^{-8}	3.456×10^5	186.0	1.44
1.84×10^{-8}	3.456×10^5	184.0	1.82
1.71×10^{-8}	3.456×10^5	171.0	2.18
1.72×10^{-8}	3.456×10^5	172.0	2.54

TABLE C-13. PERMEABILITY HISTORY FOR THE CALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ACETONE (PORE VOLUME = 455 cm^3; HYDRAULIC GRADIENT = 361.6)

K ($cm\ sec^{-1}$)	T (sec)	Volume (mls)	Pore Volume
2.82×10^{-9}	6.912×10^5	56.5	0.46
3.44×10^{-9}	6.912×10^5	69.0	0.33
4.14×10^{-9}	6.912×10^5	83.0	0.18
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Acetone			0.0
4.32×10^{-9}	6.912×10^5	86.5	0.19
3.27×10^{-9}	6.912×10^5	65.5	0.33
9.99×10^{-9}	8.640×10^4	25.0	0.39
1.12×10^{-8}	8.640×10^4	28.0	0.45
$>4.00 \times 10^{-7}$	8.640×10^4	>1000*	>2.65

* Entire volume of the fluid chamber (∿1 liter) was released within one sampling period (24 hrs) resulting in air blowing through the core.

TABLE C-14. PERMEABILITY HISTORY FOR THE CALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY METHANOL (PORE VOLUME = 454 cm^3; HYDRAULIC GRADIENT = 361.6)

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
4.70×10^{-9}	6.912×10^5	94.0	0.39
5.43×10^{-9}	5.184×10^5	81.5	0.18
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Methanol			0.0
5.12×10^{-9}	6.912×10^5	102.5	0.22
5.19×10^{-9}	8.640×10^4	13.0	0.25
$>4.0 \times 10^{-7}$	8.640×10^4	>1000*	>2.45

* Entire volume of the fluid chamber (~1 liter) was released within one sampling period (24 hrs) resulting in air blowing through the core.

TABLE C-15. PERMEABILITY HISTORY FOR THE CALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY XYLENE (PORE VOLUME = 478 cm^3; HYDRAULIC GRADIENT = 361.6)

Effluent		K	T	Volume	Pore
H_2O(%)	Xylene(%)	(cm sec^{-1})	(sec)	(mls)	Volume
100	0	5.54×10^{-9}	6.912×10^{5}	111.5	0.41
100	0	5.69×10^{-9}	5.184×10^{5}	85.5	0.18
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Xylene					0.0
100	0	5.40×10^{-9}	3.456×10^{5}	54.0	0.11
100	0	4.79×10^{-9}	8.640×10^{4}	12.0	0.14
∿26	∿74	1.70×10^{-8}	8.640×10^{4}	42.5	0.23
∿14	∿86	4.58×10^{-8}	5.280×10^{3}	7.0	0.24
Trace	∿100	4.43×10^{-6}	3.600×10^{3}	462.0	1.21

TABLE C-16. PERMEABILITY HISTORY FOR THE CALCAREOUS SMETITIC CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY HEPTANE (PORE VOLUME = 443 cm^3; HYDRAULIC GRADIENT = 361.6)

Effluent		K	T	Volume	Pore
H_2O(%)	Heptane(%)	(cm sec^{-1})	(sec)	(mls)	Volume
100	0	3.37×10^{-9}	6.912×10^5	67.5	0.28
100	0	3.90×10^{-9}	5.184×10^5	58.5	0.13
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Heptane					0.0
100	0	3.86×10^{-9}	5.184×10^5	58.0	0.13
∿35	∿65	1.02×10^{-8}	8.640×10^4	25.5	0.19
Trace	∿100	2.81×10^{-8}	4.920×10^3	4.0	0.20
∿4	∿96	2.48×10^{-7}	3.900×10^3	28.0	0.26
Trace	∿100	1.76×10^{-7}	8.640×10^4	440.0	1.25
Trace	∿100	1.73×10^{-7}	8.640×10^4	432.0	2.23

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TABLE C-17. PERMEABILITY HISTORY FOR THE MIXED CATION KAOLINITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) (CONTROL)

(PORE VOLUME = 395 cm^3; HYDRAULIC GRADIENT = 61.1)

K ($cm\ sec^{-1}$)	T (sec)	Volume (mls)	Pore Volume
2.04×10^{-8}	1.602×10^5	16.0	0.14
1.79×10^{-8}	1.765×10^5	15.5	0.10
1.90×10^{-8}	2.475×10^5	25.0	0.06
"Fluid In" continued with H_2O (0.01N $CaSO_4$)			0.0
2.35×10^{-8}	6.912×10^5	79.6	0.20
2.47×10^{-8}	6.912×10^5	83.5	0.41
2.56×10^{-8}	6.912×10^5	86.6	0.63
2.43×10^{-8}	6.912×10^5	82.1	0.84
2.76×10^{-8}	6.912×10^5	93.3	1.08
2.23×10^{-8}	6.912×10^5	75.6	1.27
2.06×10^{-8}	6.912×10^5	69.7	1.44
2.05×10^{-8}	6.912×10^5	69.4	1.62
2.06×10^{-8}	5.184×10^5	52.2	1.75

TABLE C-18. PERMEABILITY HISTORY FOR THE MIXED CATION KAOLINITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ACETIC ACID

(PORE VOLUME = 381 cm^3; HYDRAULIC GRADIENT = 61.1)

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
1.27×10^{-8}	3.367×10^5	21.0	0.10
1.32×10^{-8}	2.475×10^5	16.0	0.04
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Acetic Acid			0.0
9.78×10^{-9}	6.912×10^5	33.1	0.09
3.64×10^{-9}	6.912×10^5	12.3	0.12
3.55×10^{-9}	6.912×10^5	12.0	0.15
3.40×10^{-9}	6.912×10^5	11.5	0.18
3.58×10^{-9}	6.912×10^5	12.1	0.21
2.30×10^{-9}	6.912×10^5	7.8	0.23
3.58×10^{-9}	6.912×10^5	12.1	0.26
1.98×10^{-9}	6.912×10^5	6.7	0.28
$<1.0 \times 10^{-11}$	1.382×10^6	0	0.28

TABLE C-19. PERMEABILITY HISTORY FOR THE MIXED CATION KAOLINITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ANILINE (PORE VOLUME = 395 cm^3; HYDRAULIC GRADIENT = 61.1)

Effluent		K	T	Volume	Pore
H_2O(%)	Aniline(%)	(cm sec^{-1})	(sec)	(mls)	Volume
100	0	1.52×10^{-8}	3.367×10^{5}	25.0	0.11
100	0	1.49×10^{-8}	2.475×10^{5}	18.0	0.04
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Aniline					0.0
100	0	1.09×10^{-8}	6.912×10^{5}	36.9	0.09
100	0	1.47×10^{-8}	6.912×10^{5}	49.8	0.22
100	0	2.06×10^{-8}	6.912×10^{5}	69.7	0.40
100	0	2.21×10^{-8}	6.912×10^{5}	74.8	0.58
$\sim$100	Trace	2.90×10^{-8}	6.912×10^{5}	98.1	0.83
$\sim$90	$\sim$10	5.68×10^{-8}	1.728×10^{5}	48.0	0.96
<10	<90	9.66×10^{-8}	1.728×10^{5}	81.7	1.16
Trace	$\sim$100	1.05×10^{-7}	1.728×10^{5}	89.0	1.39
Trace	$\sim$100	1.00×10^{-7}	3.456×10^{5}	170.0	1.82
Trace	$\sim$100	2.51×10^{-7}	1.668×10^{5}	205.0	2.34
Trace	$\sim$100	3.17×10^{-7}	1.206×10^{4}	18.7	2.38

TABLE C-20. PERMEABILITY HISTORY FOR THE MIXED CATION KAOLINITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ETHYLENE GLYCOL

(PORE VOLUME = 408 cm^3; HYDRAULIC GRADIENT = 61.1)

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
1.52×10^{-8}	3.367×10^5	25.0	0.11
1.57×10^{-8}	2.475×10^5	19.0	0.05
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Ethylene Glycol			0.0
1.68×10^{-8}	6.912×10^5	56.7	0.14
9.64×10^{-9}	6.912×10^5	32.6	0.22
5.44×10^{-9}	6.912×10^5	18.4	0.27
4.17×10^{-9}	6.912×10^5	14.1	0.30
4.76×10^{-9}	6.912×10^5	16.1	0.34
4.52×10^{-9}	6.912×10^5	15.3	0.38
5.65×10^{-9}	6.912×10^5	19.1	0.43
4.38×10^{-9}	6.912×10^5	14.8	0.47
3.31×10^{-9}	6.912×10^5	11.2	0.50
2.54×10^{-9}	6.912×10^5	8.6	0.52
2.36×10^{-9}	8.640×10^4	1.0	0.52

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TABLE C-21. PERMEABILITY HISTORY FOR THE MIXED CATION KAOLINITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ACETONE (PORE VOLUME = 408 cm^3; HYDRAULIC GRADIENT = 61.1)

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
1.91×10^{-8}	1.602×10^5	15.0	0.14
1.97×10^{-8}	1.765×10^5	17.0	0.10
2.15×10^{-8}	2.475×10^5	26.0	0.06
"Fluid In" changed from H_2O (0.01N $CaSO_4$) Acetone			0.0
2.77×10^{-8}	3.456×10^5	46.9	0.11
2.06×10^{-8}	3.456×10^5	34.8	0.20
1.31×10^{-8}	3.456×10^5	22.2	0.25
1.24×10^{-8}	3.456×10^5	21.0	0.31
1.43×10^{-8}	3.456×10^5	24.2	0.36
2.14×10^{-8}	3.456×10^5	36.2	0.45
3.74×10^{-8}	1.728×10^5	31.6	0.53
6.15×10^{-8}	8.640×10^4	26.0	0.59
1.89×10^{-7}	4.320×10^4	40.0	0.69
3.55×10^{-7}	4.320×10^4	75.0	0.88
4.82×10^{-7}	5.360×10^4	126.5	1.19
5.26×10^{-7}	2.270×10^4	58.5	1.33

TABLE C-22. PERMEABILITY HISTORY FOR THE MIXED CATION KAOLINITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY METHANOL (PORE VOLUME = 395 cm^3; HYDRAULIC GRADIENT = 61.1)

K ($cm\ sec^{-1}$)	T (sec)	Volume (mls)	Pore Volume
1.43×10^{-8}	3.285×10^{5}	23.0	0.10
1.49×10^{-8}	2.475×10^{5}	18.0	0.04
"Fluid In" changed from H_2O (0.01N $CaSO_4$) Methanol			0.0
2.19×10^{-8}	3.456×10^{5}	37.0	0.09
1.68×10^{-8}	3.456×10^{5}	28.5	0.16
1.85×10^{-8}	3.456×10^{5}	31.3	0.24
5.44×10^{-8}	3.456×10^{5}	92.1	0.48
1.24×10^{-7}	3.456×10^{5}	209.1	1.01
1.57×10^{-7}	8.060×10^{4}	62.0	1.16
3.04×10^{-7}	7.740×10^{4}	115.0	1.46
5.02×10^{-7}	6.430×10^{4}	158.0	1.86

TABLE C-23. PERMEABILITY HISTORY FOR THE MIXED CATION KAOLINITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY XYLENE (PORE VOLUME = 384 cm^3; HYDRAULIC GRADIENT = 61.1)

Effluent		K	T	Volume	Pore
H_2O(%)	Xylene(%)	(cm sec^{-1})	(sec)	(mls)	Volume
100	0	1.78×10^{-8}	1.602×10^5	14.0	0.13
100	0	1.75×10^{-8}	1.755×10^5	15.0	0.10
100	0	1.77×10^{-8}	2.475×10^5	21.5	0.06
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Xylene					0.0
100	0	1.66×10^{-8}	3.456×10^5	28.1	0.07
∿100	Trace	2.14×10^{-8}	1.296×10^5	13.6	0.11
Trace	∿100	3.17×10^{-7}	4.320×10^4	67.0	0.28
Trace	∿100	7.66×10^{-7}	3.600×10^3	13.5	0.32
Trace	∿100	8.29×10^{-7}	3.600×10^3	14.6	0.36
Trace	∿100	9.65×10^{-7}	3.600×10^3	17.0	0.40
Trace	∿100	1.90×10^{-6}	3.600×10^3	33.5	0.49
Trace	∿100	2.36×10^{-6}	3.600×10^3	41.5	0.60

TABLE C-24. PERMEABILITY HISTORY FOR THE MIXED CATION KAOLINITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY HEPTANE (PORE VOLUME = 378 cm^3; HYDRAULIC GRADIENT = 61.1)

Effluent		K	T	Volume	Pore
H_2O(%)	Heptane(%)	(cm sec^{-1})	(sec)	(mls)	Volume
100	0	1.78×10^{-8}	1.602×10^5	14.0	0.14
100	0	1.86×10^{-8}	1.755×10^5	16.0	0.10
100	0	1.98×10^{-8}	2.475×10^5	24.0	0.06
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Heptane					0.0
100	0	3.36×10^{-8}	2.592×10^5	42.6	0.11
Trace	∿100	1.25×10^{-7}	1.728×10^5	106.1	0.39
Trace	∿100	1.64×10^{-6}	3.600×10^3	29.0	0.47
Trace	∿100	3.58×10^{-6}	1.442×10^4	252.3	1.14

TABLE C-25. PERMEABILITY HISTORY FOR THE MIXED CATION ILLITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) (CONTROL)

(PORE VOLUME = 398 cm^3; HYDRAULIC GRADIENT = 61.1)

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
1.03×10^{-9}	6.246×10^5	31.5	0.36
6.55×10^{-9}	9.576×10^5	30.7	0.28
6.19×10^{-9}	1.442×10^6	43.7	0.20
1.05×10^{-8}	6.912×10^5	35.4	0.09
"Fluid In" continued with H_2O (0.01N $CaSO_4$)			
8.46×10^{-9}	3.456×10^5	14.3	0.04
1.01×10^{-8}	6.912×10^5	34.0	0.12
1.17×10^{-8}	6.912×10^5	39.4	0.22
1.36×10^{-8}	6.912×10^5	45.9	0.34
1.07×10^{-8}	6.912×10^5	36.0	0.43
9.88×10^{-9}	6.912×10^5	33.4	0.51
1.01×10^{-8}	6.912×10^5	34.0	0.60
1.05×10^{-8}	6.912×10^5	35.4	0.68
1.24×10^{-8}	6.912×10^5	42.0	0.79
1.04×10^{-8}	6.912×10^5	35.0	0.88
1.07×10^{-8}	6.912×10^5	36.2	0.97
1.28×10^{-8}	6.912×10^5	43.3	1.08
1.09×10^{-8}	6.912×10^5	36.9	1.17
1.30×10^{-8}	6.912×10^5	43.9	1.28
1.45×10^{-8}	6.912×10^5	49.0	1.40

(Continued)

TABLE C-25. CONTINUED

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
1.48×10^{-8}	6.912×10^{5}	49.9	1.53
1.61×10^{-8}	6.912×10^{5}	54.5	1.67
1.69×10^{-8}	6.912×10^{5}	57.0	1.81
1.83×10^{-8}	6.912×10^{5}	61.9	1.96
1.99×10^{-8}	6.912×10^{5}	67.1	2.13
2.02×10^{-8}	6.912×10^{5}	68.2	2.30

TABLE C-26. PERMEABILITY HISTORY FOR THE MIXED CATION ILLITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ACETIC ACID

(PORE VOLUME = 405 cm^3; HYDRAULIC GRADIENT = 61.1)

K ($cm\ sec^{-1}$)	T (sec)	Volume (mls)	Pore Volume
7.85×10^{-9}	9.576×10^{5}	36.8	0.26
6.23×10^{-9}	1.442×10^{6}	44.0	0.17
7.84×10^{-9}	6.912×10^{5}	26.5	0.07
"Fluid In" changed from the H_2O (0.01N $CaSO_4$) to Acetic Acid			0.0
8.02×10^{-9}	6.912×10^{5}	27.1	0.07
5.83×10^{-9}	6.912×10^{5}	19.7	0.12
7.87×10^{-9}	6.912×10^{5}	26.6	0.18
7.07×10^{-9}	6.912×10^{5}	23.9	0.24
7.07×10^{-9}	6.912×10^{5}	23.9	0.30
7.93×10^{-9}	6.912×10^{5}	26.8	0.37
5.56×10^{-9}	6.912×10^{5}	18.8	0.41
5.92×10^{-9}	6.912×10^{5}	20.0	0.46
5.83×10^{-9}	6.912×10^{5}	19.7	0.51
3.85×10^{-9}	6.912×10^{5}	13.0	0.54
3.22×10^{-9}	6.912×10^{5}	10.9	0.57
1.60×10^{-9}	6.912×10^{5}	5.4	0.58
1.89×10^{-9}	6.912×10^{5}	6.4	0.60
1.48×10^{-9}	6.912×10^{5}	5.0	0.61
1.18×10^{-9}	6.912×10^{5}	4.0	0.62
7.69×10^{-10}	6.912×10^{5}	2.6	0.62

(Continued)

TABLE C-26. CONTINUED

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
9.47×10^{-10}	6.912×10^{5}	3.2	0.63
1.69×10^{-9}	6.912×10^{5}	5.7	0.65
1.83×10^{-9}	6.912×10^{5}	6.2	0.66
1.69×10^{-9}	6.912×10^{5}	5.7	0.68

TABLE C-27. PERMEABILITY HISTORY FOR THE MIXED CATION ILLITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ANILINE (PORE VOLUME = 402 cm^3; HYDRAULIC GRADIENT = 61.1)

Effluent H_2O(%)	Effluent Aniline(%)	K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
100	0	6.14×10^{-9}	2.592×10^5	7.8	0.13
100	0	2.88×10^{-9}	9.576×10^5	13.5	0.11
100	0	2.55×10^{-9}	1.442×10^6	18.0	0.08
100	0	3.91×10^{-9}	6.912×10^5	13.2	0.03
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Aniline					0.0
100	0	6.21×10^{-9}	3.456×10^5	10.5	0.03
100	0	1.21×10^{-8}	8.640×10^4	5.1	0.04
∿50	∿50	1.26×10^{-7}	4.320×10^4	26.5	0.10
∿10	∿90	1.28×10^{-7}	4.320×10^4	27.0	0.17

TABLE C-28. PERMEABILITY HISTORY FOR THE MIXED CATION ILLITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ETHYLENE GLYCOL

(PORE VOLUME = 404 cm^3; HYDRAULIC GRADIENT = 61.1)

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
7.17×10^{-9}	1.710×10^5	6.0	0.28
8.47×10^{-9}	4.536×10^6	18.8	0.26
5.31×10^{-9}	9.576×10^5	24.9	0.21
5.03×10^{-9}	1.442×10^6	35.5	0.15
7.78×10^{-9}	6.912×10^5	26.3	0.07
"Fluid In" changed from the H_2O (0.01N $CaSO_4$) to Ethylene Glycol			0.0
8.05×10^{-9}	6.912×10^5	27.2	0.07
7.28×10^{-9}	6.912×10^5	24.6	0.13
7.69×10^{-9}	6.912×10^5	26.0	0.19
5.50×10^{-9}	6.912×10^5	18.6	0.24
4.64×10^{-9}	6.912×10^5	15.7	0.28
3.82×10^{-9}	6.912×10^5	12.9	0.31
3.55×10^{-9}	6.912×10^5	12.0	0.34
3.11×10^{-9}	6.912×10^5	10.5	0.37
3.99×10^{-9}	6.912×10^5	13.5	0.40
2.87×10^{-9}	6.912×10^5	9.7	0.42
2.40×10^{-9}	6.912×10^5	8.1	0.44
2.19×10^{-9}	6.912×10^5	7.4	0.46
1.98×10^{-9}	6.912×10^5	6.7	0.48
2.81×10^{-9}	6.912×10^5	9.5	0.50

(Continued)

TABLE C-28. CONTINUED

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
1.51×10^{-9}	6.912×10^{5}	5.1	0.51
9.76×10^{-10}	6.912×10^{5}	3.3	0.52
1.51×10^{-9}	6.912×10^{5}	5.1	0.53
1.57×10^{-9}	6.912×10^{5}	5.3	0.55
1.48×10^{-9}	6.912×10^{5}	5.0	0.56
1.63×10^{-9}	6.912×10^{5}	5.5	0.57
1.57×10^{-9}	6.912×10^{5}	5.3	0.59

TABLE C-29. PERMEABILITY HISTORY FOR THE MIXED CATION ILLITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY ACETONE (PORE VOLUME = 399 cm^3; HYDRAULIC GRADIENT = 61.1)

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
2.57×10^{-9}	3.024×10^{6}	38.0	0.12
3.55×10^{-9}	6.912×10^{5}	12.0	0.03
"Fluid In" changed from the H_2O (0.01N $CaSO_4$) to Acetone			0.0
6.89×10^{-9}	6.912×10^{5}	23.3	0.06
5.77×10^{-9}	6.912×10^{5}	19.5	0.11
5.53×10^{-9}	6.912×10^{5}	18.7	0.15
4.73×10^{-9}	6.912×10^{5}	16.0	0.19
4.14×10^{-9}	6.912×10^{5}	14.0	0.23
3.85×10^{-9}	6.912×10^{5}	13.0	0.26
3.37×10^{-9}	6.912×10^{5}	11.4	0.29
3.52×10^{-9}	6.912×10^{5}	11.9	0.32
4.50×10^{-9}	6.912×10^{5}	15.2	0.36
3.43×10^{-9}	6.912×10^{5}	11.6	0.39
3.55×10^{-9}	6.912×10^{5}	12.0	0.42
4.67×10^{-9}	6.912×10^{5}	15.8	0.46
1.43×10^{-8}	1.728×10^{5}	12.1	0.49
2.38×10^{-8}	1.728×10^{5}	20.1	0.54
3.90×10^{-8}	1.728×10^{5}	33.0	0.62
8.45×10^{-8}	1.728×10^{5}	71.5	0.80
1.17×10^{-8}	2.160×10^{4}	124.1	1.11

(Continued)

TABLE C-29. CONTINUED

K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
7.96×10^{-7}	1.080×10^{4}	42.1	1.22
8.24×10^{-7}	3.600×10^{3}	14.5	1.25
8.41×10^{-7}	3.600×10^{3}	14.8	1.29
8.92×10^{-7}	3.600×10^{3}	15.7	1.33

TABLE C-30. PERMEABILITY HISTORY FOR THE MIXED CATION ILLITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY METHANOL

(PORE VOLUME = 408 cm^3; HYDRAULIC GRADIENT = 61.1*)

Effluent H_2O(%)	Effluent Methanol(%)	K (cm sec^{-1})	T (sec)	Volume (mls)	Pore Volume
100	0	7.40×10^{-9}	2.592×10^{5}	9.4	0.20
100	0	4.31×10^{-9}	9.576×10^{5}	20.2	0.17
100	0	4.28×10^{-9}	1.442×10^{6}	30.2	0.13
100	0	6.18×10^{-9}	6.912×10^{5}	20.9	0.05
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Methanol					0.0
100	0	6.89×10^{-9}	6.912×10^{5}	23.3	0.06
100	0	5.74×10^{-9}	6.912×10^{5}	19.4	0.10
100	0	6.39×10^{-9}	6.912×10^{5}	21.6	0.16
100	0	5.44×10^{-9}	6.912×10^{5}	18.4	0.20
100	0	5.65×10^{-9}	6.912×10^{5}	19.1	0.25
100	0	6.66×10^{-9}	6.912×10^{5}	22.5	0.30
100	Trace	9.23×10^{-9}	6.912×10^{5}	31.2	0.38
97	3	2.16×10^{-8}	3.456×10^{5}	36.5	0.47
66	34	3.60×10^{-8}	3.456×10^{5}	60.8	0.62
47	53	5.45×10^{-8}	2.592×10^{5}	69.2	0.79
39	61	7.38×10^{-8}	8.640×10^{4}	31.2	0.87
34	66	1.19×10^{-7}	8.640×10^{4}	50.2	0.99
29	71	1.96×10^{-7}	8.640×10^{4}	83.1	1.19
24	76	2.96×10^{-7}	4.320×10^{4}	62.5	1.35
21	79	3.19×10^{-7}	2.160×10^{4}	33.8	1.43

(Continued)

TABLE C-30. CONTINUED

Effluent		K	T	Volume	Pore
H_2O(%)	Methanol(%)	(cm sec^{-1})	(sec)	(mls)	Volume
21	79	3.96×10^{-7}	2.160×10^{4}	42.0	1.53
21	79	5.19×10^{-7}	2.160×10^{4}	55.0	1.67
ND	ND	9.76×10^{-8}	6.912×10^{5}	10.0	1.69
ND	ND	1.67×10^{-7}	6.912×10^{5}	17.1	1.74
ND	ND	3.55×10^{-7}	6.912×10^{5}	36.4	1.83
ND	ND	6.66×10^{-7}	6.912×10^{5}	68.2	1.99
ND	ND	1.66×10^{-6}	2.590×10^{5}	63.7	2.15
ND	ND	2.43×10^{-6}	1.728×10^{5}	62.1	2.30
ND	ND	4.78×10^{-6}	2.160×10^{4}	15.3	2.34
ND	ND	1.19×10^{-5}	2.160×10^{4}	38.1	2.43
ND	ND	1.65×10^{-5}	2.160×10^{4}	52.7	2.56

ND = Not determined.

Hydraulic gradient (H) changed from 61.1 to 1.85 at PV = 1.67.

TABLE C-31. PERMEABILITY HISTORY FOR THE MIXED CATION ILLITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY XYLENE (PORE VOLUME = 405 cm^3; HYDRAULIC GRADIENT = 61.1)

Effluent		K	T	Volume	Pore
H_2O(%)	Xylene(%)	(cm sec^{-1})	(sec)	(mls)	Volume
100	0	3.35×10^{-9}	1.710×10^{5}	2.8	0.14
100	0	5.41×10^{-9}	4.536×10^{5}	12.0	0.14
100	0	2.54×10^{-9}	9.576×10^{5}	11.9	0.11
100	0	2.76×10^{-9}	1.442×10^{6}	19.5	0.08
100	0	3.49×10^{-9}	6.912×10^{5}	11.8	0.03
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Xylene					0.0
100	0	7.34×10^{-9}	3.456×10^{5}	12.4	0.03
∿58	∿42	8.25×10^{-8}	4.320×10^{4}	17.4	0.07
Trace	∿100	1.33×10^{-7}	4.320×10^{4}	28.0	0.14
Trace	∿100	2.61×10^{-6}	1.800×10^{3}	23.0	0.20
Trace	∿100	2.61×10^{-6}	1.800×10^{3}	23.0	0.26
Trace	∿100	2.27×10^{-6}	1.800×10^{3}	20.0	0.31
Trace	∿100	1.65×10^{-6}	3.600×10^{3}	29.0	0.38

TABLE C-32. PERMEABILITY HISTORY FOR THE MIXED CATION ILLITE CLAY SOIL PERMEATED WITH H_2O (0.01N $CaSO_4$) FOLLOWED BY HEPTANE

(PORE VOLUME = 413 cm^3; HYDRAULIC GRADIENT = 61.1)

Effluent		K	T	Volume	Pore
H_2O(%)	Heptane(%)	(cm sec^{-1})	(sec)	(mls)	Volume
100	0	4.78×10^{-9}	9.576×10^{5}	22.4	0.15
100	0	3.12×10^{-9}	1.442×10^{6}	22.0	0.09
100	0	4.88×10^{-9}	6.912×10^{5}	16.5	0.04
"Fluid In" changed from H_2O (0.01N $CaSO_4$) to Heptane					0.0
100	0	5.71×10^{-9}	5.184×10^{5}	14.5	0.04
∿50	∿50	5.88×10^{-8}	4.320×10^{4}	12.4	0.07
Trace	∿100	4.20×10^{-6}	1.800×10^{3}	37.0	0.15
Trace	∿100	4.77×10^{-6}	1.800×10^{3}	42.0	0.26
Trace	∿100	5.11×10^{-6}	1.800×10^{3}	45.0	0.37
Trace	∿100	5.63×10^{-6}	3.600×10^{3}	99.0	0.61
Trace	∿100	5.80×10^{-6}	3.600×10^{3}	102.0	0.85
Trace	∿100	6.53×10^{-6}	3.600×10^{3}	115.0	1.13
Trace	∿100	6.46×10^{-6}	2.100×10^{3}	66.5	1.29
Trace	∿100	4.02×10^{-6}	6.600×10^{3}	130.0	1.61